

### **REMARKS**

Claims 1-35 remain pending in the application, all of which stand rejected. The amendment to the specification finds support in original claim 3. No new matter is added.

Applicants note that the Zimmerman et al. reference (U.S. Patent no. 4,845,583) is not listed on any PTO-892 or PTO/SB/08A, and is therefore not officially of record in the present application. Applicants request the Examiner to provide a PTO-892 listing Zimmerman et al. with the next Office Action.

#### **Rejection under 35 U.S.C. §112**

Claim 3 is rejected under 35 U.S.C. §112, first paragraph for a lack of support in the specification. The amendment to the specification should moot this ground of rejection.

#### **Rejection under 35 U.S.C. §103(a) over Carroll et al. in view of Drelich**

Claims 1, 2, 4-6, 14-19, 28-31, 34 and 35 are rejected under 35 U.S.C. §103(a) as obvious over Carroll et al. (WO 97/45259) in view of Drelich (U.S. Patent no. 2,880,113). Applicants traverse this basis for rejection and respectfully request reconsideration and withdrawal thereof.

#### ***Nature Of The Present Invention***

In a first embodiment, the present invention is directed to a moisture vapor permeable, substantially liquid impermeable composite sheet material comprising a moisture vapor permeable monolithic polymeric film comprising a polymer selected from the group consisting of a block polyether ester copolymer, a poly(etherimide) ester copolymer, or a combination thereof, having a first side and a second side, and a first nonwoven layer comprising a moisture vapor permeable powder-bonded nonwoven layer, said powder-bonded layer comprising a nonwoven web of fibers, *wherein greater than 95 weight percent of the fibers in the nonwoven web are compatible with said polymeric film*, said first nonwoven layer being adhered to the first side of the polymeric film by extrusion of said film onto said first nonwoven layer. (Claim 1, emphasis added).

### ***The Prior Art***

Carroll et al. disclose a breathable composite sheet material comprised of a thermoplastic film adhered directly to a fibrous substrate, wherein the film comprises at least 50% by weight of a polymer material from the group of block copolyether esters, block copolyether amides and polyurethanes. The substrate comprises a fibrous web of at least 50% by weight of polyolefin polymer synthetic fibers. (Abstract).

As recognized by the Examiner, Carroll et al. fail to disclose that the substrate should be a powder bonded nonwoven layer. (Office Action, page 4).

Drelich discloses a durable nonwoven fabric which comprises a multiplicity of relatively small granule bonds of heat fused material distributed approximately uniformly in a layer of overlapping and intersecting fibers (col. 2, lines 3-8). The "granule bonds" of Drelich are formed by distributing granules of a suitable binder in the fibrous layer and subsequently applying heat and pressure to the fibrous layer to fuse the binder material to the fibers (col. 5, lines 5-22).

Drelich discloses fabrics formed of natural fibers such as cotton and wood or artificial fibers, such as regenerated cellulose, nylon and viscose rayon (col. 7, lines 1-10). Drelich exemplifies only fabrics made of viscose rayon.

### ***The Proposed Combination of References***

The Examiner has suggested that it would have been obvious to modify the Carroll et al. laminate to use the powder bonded nonwoven fabric of Drelich (Office Action, page 5). Applicants traverse the Examiner's proposed combination as failing to establish a prima facie case of obviousness as to the present claims.

It is important to note that according to claim 1, "...greater than 95 weight percent of the fibers in the nonwoven web are compatible with said polymeric film...", and that the polymeric film is limited to those "...comprising a polymer selected from the group consisting of a block polyether ester copolymer, a poly(etherimide) ester copolymer, or a combination thereof...".

Applicants respectfully submit that the powder bonded fabrics disclosed or suggested by Drelich would not be compatible with the films designated by claim 1, and therefore, even if combined according to the manner suggested by the Examiner,

the hypothetical laminate would not meet the limitations of the present claims. More importantly, those of skill in the art would not have an expectation of success in substituting the incompatible fabrics of Drelich for those of Carroll et al.

To establish a *prima facie* case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references when combined) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based on the applicant's disclosure. MPEP § 2142, citing *In re Vaeck*, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991).

Thus, the Examiner's proposed combination fails to establish a *prima facie* case of obviousness, in view of the second and third prongs of the test set forth in *In re Vaeck*.

In support of their position that the Drelich fabrics would be incompatible with the claimed films of the present invention, Applicants direct attention to the definition of "compatibility" and "compatible" as set forth at page 4, line 30, bridging to page 5 of the specification. In order for polymers to be considered compatible, they must be miscible. The presently claimed films contain ester linkages in their polymer backbones, which would not be expected to be miscible/compatible with the cellulosic or polyamide fibers disclosed by Drelich, merely based upon the well-known chemical rubric of "like dissolves like" (Rosen, Fundamental Principles of Polymeric Materials, second edition (1993), pp. 83-84; attached hereto).

On a more rigorous basis, polymer compatibility/miscibility can be predicted through the comparison of the solubility parameters of the various polymers. Generally, solubility of polymers in various media is determined, in theory, on the Gibbs free energy equation, which indicates that solubility occurs when the free energy of mixing is negative:

$$\Delta G = \Delta H - T\Delta S,$$

discussed in detail at pp. 152-157 of Billmeyer, Jr., Textbook of Polymer Science, third edition (1984); copy attached. Generally, Billmeyer indicates that the difference

in solubility parameters of a solvent and a polymer should be small, e.g. less than 4  $(\text{J}/\text{cm}^3)^{1/2}$ .

Compatibilities of polymer/polymer systems raise additional factors to be considered, such as molecular weights, dispersive interactions and dipole-dipole interactions; but solubility parameters can be used to predict blend compatibility and phase separation (Billmeyer, Jr., pp. 175-176). Overall, the smaller the differences in solubility parameters the more compatible the polymers. The Polymer Handbook, third edition (1989) (copy attached) indicates a solubility parameter for cellulose (rayon, cotton, etc) of 32.02  $(\text{MPa})^{1/2}$  (page 555), and for nylons an average of about 23.8  $(\text{MPa})^{1/2}$  (page 556); the two fabric materials specifically disclosed in Drelich. While the commercial literature does not appear to report solubility parameters for the polymers of the presently claimed film layers, Applicants have calculated an average value for its Hytrel® polymers: about 18.2  $(\text{MPa})^{1/2}$ . Accordingly, the difference in solubility parameters between Drelich's cellulose and Hytrel® is about 13.8  $(\text{MPa})^{1/2}$ , and between nylon and Hytrel® about 5.6  $(\text{MPa})^{1/2}$ . In contrast, the solubility parameter difference between Hytrel® and a disclosed compatible polymer fiber, polyethylene terephthalate (specification, page 7, lines 26-27) is about 3.33  $(\text{MPa})^{1/2}$ , based upon the solubility parameter for polyethylene terephthalate of 21.54  $(\text{MPa})^{1/2}$  (Polymer Handbook, page 556).

Accordingly, Applicants submit that the fabrics suggested by Drelich are not "compatible" with the polymeric films of claim 1 of the present application. Withdrawal of the rejection is requested for failure to establish a *prima facie* case of obviousness.

**Rejection under 35 U.S.C. §103(a) over Carroll et al.**  
**in view of Drelich**

Claims 12 and 13 are rejected under 35 U.S.C. §103(a) as obvious over Carroll et al. in view of Drelich. Applicants traverse this basis for rejection and respectfully request reconsideration and withdrawal thereof.

Applicants reiterate their comments in traverse of the combination of Drelich and Carroll et al., as set forth above. The skilled artisan would not have had an expectation of success in combining the fabric of Drelich and the films of Carroll et al.

Withdrawal of the rejection for failure to establish a *prima facie* case of obviousness is requested.

**Rejection under 35 U.S.C. §103(a) over Carroll et al.**  
**in view of Drelich and further in view of Zimmerman et al.**

Claims 7 and 8 are rejected under 35 U.S.C. §103(a) as obvious over Carroll et al. in view of Drelich, and further in view of Zimmerman et al. (U.S. 4,845,583). Applicants traverse this basis for rejection and respectfully request reconsideration and withdrawal thereof.

Applicants reiterate their comments in traverse of the combination of Drelich and Carroll et al., as set forth above. The Examiner apparently cites Zimmerman et al. for the proposition that it would have been obvious to substitute a powder-bonded polyethylene terephthalate nonwoven fabric for those of Drelich. The Examiner states:

Since Carroll et al., Drelich and Zimmerman et al. *are from the same field of endeavor*, the purpose disclosed by Zimmerman et al. would have been recognized in the pertinent art of Carroll et al. and Drelich. (Office Action, page 6, emphasis added).

Applicants respectfully submit that the Examiner's suggestion that Zimmerman et al. and the other references "are from the same field of endeavor" truly stretches the concept of analogous art beyond its breaking point. Carroll et al. disclose breathable composite sheets, such as diapers (Abstract), which require air and moisture vapor permeability. Likewise, Drelich discloses fabrics which would be suitable for use in making, among others, sanitary napkins (col. 1, line 71), which is at least somewhat related to the field of use disclosed by Carroll et al. In contrast, Zimmerman et al. disclose fabric jackets for floppy diskettes, which is certainly non-analogous to the uses disclosed by Carroll et al. and Drelich. Zimmerman et al. neither disclose nor suggest any reason that the diskette jackets be permeable to air and moisture, nor that they would benefit a human wearer in any manner whatsoever. Further, neither Carroll et al. nor Drelich disclose a reason to use "cutouts", disclosed by Zimmerman et al., in the uses of their fabrics, which would motivate a skilled artisan to look to Zimmerman et al. for a way to improve fiber retention.

In fact, the only connection between the three cited references is that each discloses a nonwoven fabric. Applicants submit that this is hardly enough to find the references to be "analogous" within the meaning of the patent law. Withdrawal of the rejection for failure to establish a *prima facie* case of obviousness, in view of an improper combination of non-analogous references, is requested.

**Rejection under 35 U.S.C. §103(a) over Carroll et al.**

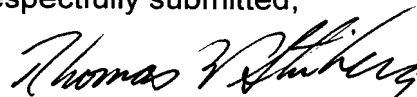
**in view of Drelich**

Claims 20-27 and 32-33 are rejected under 35 U.S.C. §103(a) as obvious over Carroll et al. in view of Drelich. Applicants traverse this basis for rejection and respectfully request reconsideration and withdrawal thereof.

Applicants reiterate their comments in traverse of the combination of Drelich and Carroll et al., as set forth above. The skilled artisan would not have had an expectation of success in combining the fabric of Drelich and the films of Carroll et al. Withdrawal of the rejection for failure to establish a *prima facie* case of obviousness is requested.

In view of the foregoing, allowance of the above-referenced application is respectfully requested.

Respectfully submitted,



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TWS:

Enclosures

- Rosen, Stephen L., Fundamental Principles of Polymeric Materials, second edition (1993), pp. 82-93.
- Billmeyer, Jr., Fred. W., Textbook of Polymer Science, third edition (1984), pp.152-157 and 168-177.
- Brandrup, J. and Immergut, E.H., Polymer Handbook, third edition (1989), pp. 519-526; 544-559.



# Fundamental Principles of Polymeric Materials

Second Edition

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## CHAPTER VII

# Polymer Solubility and Solutions

### 7.1 INTRODUCTION

The thermodynamics and statistics of polymer solutions is an interesting and important branch of physical chemistry, and is the subject of many good books and large sections of books in itself. It is far beyond the scope of this chapter to attempt to cover the subject in detail. Instead, we will concentrate on topics of practical interest and try to indicate, at least qualitatively, their fundamental bases. Three factors are of general interest:

1. What solvents will dissolve what polymers?
2. How do the interactions between polymer and solvent influence the properties of the solution?
3. To what applications do the interesting properties of polymer solutions lead?

### 7.2 TYPICAL PHASE BEHAVIOR IN POLYMER-SOLVENT SYSTEMS

Figure 7.1 shows schematically a phase diagram for a typical polymer-solvent system, plotting temperature vs. the fraction polymer in the system. At low temperatures, a two-phase system is formed. The dotted tie lines connect the compositions of phases in equilibrium, a solvent-rich (dilute-solution) phase on the left and a polymer-rich (swollen-polymer or gel) phase on the right. As the temperature is raised, the compositions of the phases become more nearly alike, until at the upper critical solution temperature (UCST) they are identical. Above the UCST, the system forms homogeneous (single-phase) solutions across the entire composition range. The location of the phase boundary depends on the

Figure 7.1 Schematic phase diagram for a polymer-solvent system. (a) swollen polymer phase; (b) swollen polymer phase; LCST, lower critical solution temperature.

molecular weight solvent.

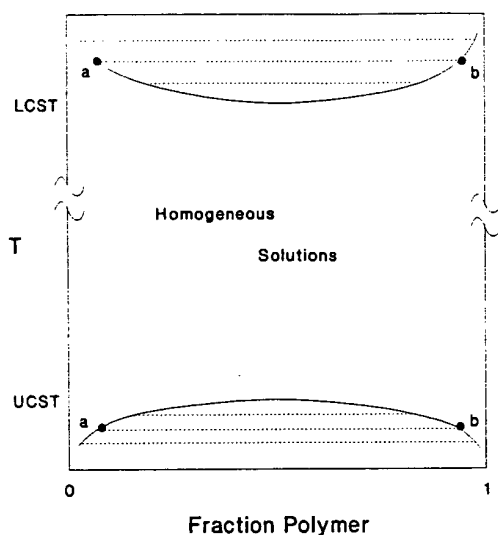
In recent years a lower critical solution temperature (LCST) has been questioned the normal way it is). LCSTs lie well above the

When we talk generally mean that forms homogeneous however, that has the composition

### 7.3 GENERAL

Let's begin by discussing polymers:

1. Like dissolves like: polymers and solvents. Chemical structure is important.



**Figure 7.1** Schematic phase diagram for polymer-solvent system: (a) dilute solution phase; (b) swollen polymer or "gel" phase. UCST, upper critical solution temperature; LCST, lower critical solution temperature.

molecular weight of the polymer and the interaction between the polymer and solvent.

In recent years, a number of systems have been examined that also exhibit a lower critical solution temperature (LCST), as shown in Fig. 7.1. (One might question the nomenclature that puts the LCST *above* the UCST, but that's the way it is). LCSTs are more difficult to observe experimentally because they often lie well above the normal boiling points of the solvents.

When we talk about a polymer being soluble in particular solvent, we generally mean that the system lies between its LCST and UCST; that is, it forms homogeneous solutions over the entire composition range. Keep in mind, however, that homogeneous solutions can still be formed toward the extremes of the composition range below the UCST and above the LCST.

### 7.3 GENERAL RULES FOR POLYMER SOLUBILITY

Let's begin by listing some general qualitative observations on the dissolution of polymers:

1. Like dissolves like; that is, polar solvents will tend to dissolve polar polymers and nonpolar solvents will tend to dissolve nonpolar polymers. Chemical similarity of polymer and solvent is a fair indication of solubility;

for example, polyvinyl alcohol,  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{---C---C---} \\ | \quad | \\ \text{H} \quad \text{O-H} \end{array}_x$ , will dissolve in water,  $\text{H-O-H}$ ,

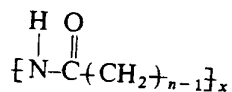
and polystyrene,  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{---C---C---} \\ | \quad | \\ \text{H} \quad \phi \end{array}_x$ , in toluene,  $\phi\text{-CH}_3$ , but toluene won't dissolve

polyvinyl alcohol and water won't dissolve polystyrene (which is good news for those of us who drink coffee out of foamed polystyrene cups).

2. In a given solvent at a particular temperature, the solubility of a polymer will decrease with increasing molecular weight.
3. a. Crosslinking eliminates solubility.
- b. Crystallinity, in general, acts like crosslinking, but it is possible in some cases to find solvents strong enough to overcome the crystalline bonding forces and dissolve the polymer. Heating the polymer toward its crystalline melting point allows its solubility in appropriate solvents. For example, nothing dissolves polyethylene at room temperature. At  $100^\circ\text{C}$ , however, it will dissolve in a variety of aliphatic, aromatic, and chlorinated hydrocarbons.
4. The rate of polymer solubility decreases with increasing molecular weight. For reasonably high molecular weight polymers, it can be orders of magnitude slower than that for nonpolymeric solutes.

It is important to note here that items 1, 2, and 3 are *equilibrium* phenomena and are therefore describable thermodynamically (at least in principle), while item 4 is a *rate* phenomenon and is governed by the rates of diffusion of polymer and solvent.

**Example 1.** The polymers of  $\omega$ -amino acids are termed "nylon  $n$ ," where  $n$  is the number of consecutive carbon atoms in the chain. Their general formula is



The polymers are crystalline, and will not dissolve in either water or hexane at room temperature. They will, however, reach an equilibrium level of absorption when immersed in each liquid. Describe how and why water and hexane absorption will vary with  $n$ .

**Solution.** Water is highly polar liquid; hexane is nonpolar. The polarity of the nylons depends on the relative proportion of polar nylon linkages  $\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{---N---C---} \end{array}$  in the chains. As  $n$  increases, the polarity of the chains decreases (they become more

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hydrocarbon-like), and so hexane absorption increases with  $n$  and water absorption decreases.

#### 7.4 THE THERMODYNAMIC BASIS OF POLYMER SOLUBILITY

"To dissolve or not to dissolve. That is the question." (with apologies to W.S.). The answer is determined by the sign of the Gibbs free energy. Consider the process of mixing pure polymer and pure solvent (state 1) at constant pressure and temperature to form a solution (state 2):

$$\Delta G = \Delta H - T\Delta S \quad (7.1)$$

where  $\Delta G$  = the change in Gibbs free energy

$\Delta H$  = the change in enthalpy

$T$  = the absolute temperature

$\Delta S$  = the change in entropy

Only if  $\Delta G$  is negative will the solution process be thermodynamically feasible. The absolute temperature must be positive, and the change in entropy for a solution process is generally positive, because in a solution, the molecules are in a more random state in the solid (this might not always be the case with lyotropic liquid-crystal materials). The positive product is preceded by a negative sign. Thus, the third ( $-T\Delta S$ ) term in (7.1) favors solubility. The change in enthalpy may be either positive or negative. A positive  $\Delta H$  means the solvent and polymer "prefer their own company," that is, the pure materials are in a lower energy state, while a negative  $\Delta H$  indicates that the solution is the lower energy state. If the latter obtains, solution is assured. Negative  $\Delta H$ 's usually arise where specific interactions such as hydrogen bonds are formed between the solvent and polymer molecules. But, if  $\Delta H$  is positive, then  $\Delta H < T\Delta S$  if the polymer is to be soluble.

One of the things that makes polymers unusual is that the entropy change in forming a polymer solution is generally much smaller than that which occurs on dissolution of equivalent masses or volumes of low molecular weight solutes. The reasons for this are illustrated qualitatively on a two-dimensional lattice model in Fig. 7.2. With the low molecular weight solute, the solute molecules may be distributed randomly throughout the lattice, the only restriction being that a lattice site cannot be occupied simultaneously by two (or more) molecules. This gives rise to a large number of configurational possibilities, that is, a high entropy. In the polymer solution, however, each chain segment is confined to a lattice site adjacent to the next chain segment, greatly reducing the configurational possibilities. Note also that for a given number of chain segments (equivalent masses or volumes of polymer) the more chains they are split up into, that is, the lower their molecular weight, the higher will be their entropy upon

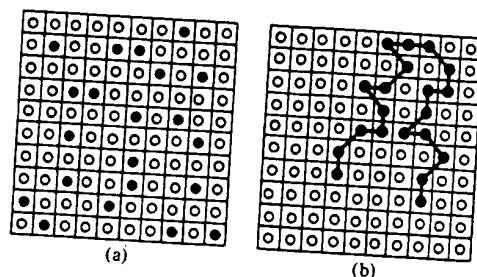


Figure 7.2 Lattice model of solubility: (a) low molecular weight solute; (b) polymeric solute. ○, Solvent; ●, Solute.

solution. This explains directly observation 2, the decrease in solubility with molecular weight. But in general, for high molecular weight polymers, because the  $T\Delta S$  term is so small, if  $\Delta H$  is positive then it must be even smaller if the polymer is to be soluble. So in the absence of specific interactions, predicting polymer solubility largely boils down to minimizing  $\Delta H$ .

## 7.5 THE SOLUBILITY PARAMETER

How can  $\Delta H$  be estimated? Well, for the formation of *regular* solutions (those in which solute and solvent do not form specific interactions), the change in *internal energy* per unit volume of solution is given by

$$\Delta H \approx \Delta E = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 [ = ] \text{ cal/cm}^3 \text{ soln} \quad (7.2)$$

where  $\Delta E$  = the change in internal energy *per unit volume of solution*

$\phi_i$  = volume fractions

$\delta_i$  = solubility parameters

The subscripts 1 and 2 usually (but not always!) refer to solvent and solute (polymer), respectively. The *solubility parameter* is defined as follows:

$$\delta = (\text{CED})^{1/2} = (\Delta E_v/v)^{1/2} \quad (7.3)$$

where CED = *cohesive energy density*, a measure of the strength of the intermolecular forces holding the molecules together in the liquid state

$\Delta E_v$  = molar change in internal energy on vaporization

$v$  = molar volume of liquid.

Traditionally, solubility parameters have been given in  $(\text{cal/cm}^3)^{1/2}$  = hildebrands (in honor of the originator of regular solution theory), but they are now more commonly listed in  $(\text{MPa})^{1/2}$  (1 hildebrand =  $0.4889 (\text{MPa})^{1/2}$ ).

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Figure 7.3 Det linked samples in

Now, for a process that occurs at constant volume and constant pressure, the changes in internal energy and enthalpy are equal. Since the change in volume on solution is usually quite small, this is a good approximation for the dissolution of polymers under most conditions, so (7.2) provides a means of estimating enthalpies of solution if the solubility parameters of the polymer and solvent are known.

Note that regardless of the magnitudes of  $\delta_1$  and  $\delta_2$  (they must be positive), the predicted  $\Delta H$  is always positive, because (7.2) applies only in the absence of the specific interactions that lead to negative  $\Delta H$ 's. Inspection of (7.2) also reveals that  $\Delta H$  is minimized, and the tendency toward solubility is therefore maximized by matching the solubility parameters as closely as possible. As a very rough rule-of-thumb (or heuristic principle, if you prefer),

$$|\delta_1 - \delta_2| < 1 \text{ (cal/cm}^3)^{1/2} \text{ for solubility} \quad (7.4)$$

Measuring the solubility parameter of a low molecular weight solvent is no problem. Polymers, on the other hand, degrade long before reaching their vaporization temperatures, making it impossible to evaluate  $\Delta E_v$  directly. Fortunately, there is a way around this impasse. The greatest tendency of a polymer to dissolve occurs when its solubility parameter matches that of the solvent. If the polymer is crosslinked lightly, it cannot dissolve, but only swell. The maximum swelling will be observed when the polymer and solvent solubility parameters are matched. So polymer solubility parameters are determined by soaking lightly crosslinked samples in a series of solvents of known solubility parameters. The value of the solvent at which maximum swelling is observed is taken as the solubility parameter of the polymer (Fig. 7.3).

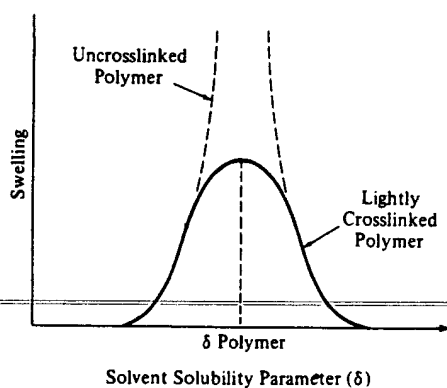


Figure 7.3 Determination of polymer solubility parameter by swelling lightly cross-linked samples in a series of solvents.

Solubility parameters of solvent mixtures can be readily calculated from

$$\delta_{\text{mix}} = \frac{\sum y_i v_i \delta_i}{\sum y_i v_i} = \sum \phi_i \delta_i \quad (7.5)$$

where  $y_i$  = mole fraction of component  $i$   
 $v_i$  = molar volume of component  $i$   
 $\phi_i$  = volume fraction of component  $i$

Equation 7.5 has often been used to prepare a series of mixed solvents for establishing the solubility parameter of a polymer as described above. Care must be exercised in this application, however, because what winds up inside the swollen polymer is not necessarily what you mixed up. In general, the cross-linked polymer will preferentially absorb the better (closer  $\delta$ ) solvent component, a phenomenon known as *coacervation*.

In the absence of specific data on solvents, a group-contribution method is available for estimating both the solubility parameters and molar volumes of liquids.<sup>1</sup>

While the solubility-parameter concept has proved useful, there are unfortunately many exceptions to (7.4). First, regular solution theory which leads to (7.2) has some shortcomings in practice. Second, polymer solubility is too complex a phenomenon to be described quantitatively with a single parameter. Several techniques have been proposed that supplement solubility parameters with quantitative information on hydrogen bonding and dipole moments.<sup>2,3</sup> One of the simplest of these classifies solvents into three categories according to their hydrogen-bonding ability (poor, moderate, strong). Three different  $\delta$  ranges are then listed for each polymer, one for each solvent category. Presumably, a solvent that falls within the  $\delta$  range for its hydrogen-bonding category will dissolve the polymer. Another technique that has achieved widespread practical application is discussed in the next section.

## 7.6 HANSEN'S THREE-DIMENSIONAL SOLUBILITY PARAMETER

According to Hansen,<sup>4-7</sup> the total change in internal energy on vaporization,  $\Delta E_v$ , may be considered the sum of three individual contributions: one due to hydrogen bonds  $\Delta E_h$ , another due to permanent dipole interactions  $\Delta E_p$ , and a third from dispersion (van der Waals or London) forces  $\Delta E_d$ :

$$\Delta E_v = \Delta E_d + \Delta E_p + \Delta E_h \quad (7.6)$$

Dividing by the molar volume  $v$  gives

$$\frac{\Delta E_v}{v} = \frac{\Delta E_d}{v} + \frac{\Delta E_p}{v} + \frac{\Delta E_h}{v} \quad (7.7)$$

or

where

Thus, the so-called three-dimensional solubility parameter  $\delta_{h1}$  is represented by this point.

A polymer found on a plot of  $\delta_{h1}$  versus  $\delta_{h2}$  that used for a sphere of radius  $R$  is soluble.

Solubility judgment based on observation of concentration changes in this is somewhat probably because of molecular weight effects.

The three-dimensional solubility parameter magnitude of the point representing the polymer is determined by the equation

$$[(\delta_{p1} - \delta_{p2})^2 + (\delta_{p3} - \delta_{p4})^2]^{1/2} = R$$

(The factor of 4 in the original equation is omitted here for a spherical solubility parameter.)

Figure 7.4 shows that solvents with  $\delta_h = 2.0$ ,  $R = 3.0$  lie outside the solubility sphere, at best.

The range of solubility in practice, therefore, is determined by the solubility parameter of the polymer.

Values of the solubility parameter  $\delta$  have been measured for a large number of compounds, and a plenty of computational methods have been published.<sup>4,5,9</sup> Mixtures of solvents according to the solubility parameter.

Despite its shortcomings, the solubility parameter has proved of great value in the choice of solvents.



culated from

(7.5)

or

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (7.8)$$

where

$$\delta_j = (\Delta E_j/v)^{1/2} \quad j = d, p, h$$

Thus, the solubility parameter  $\delta$  may be thought of as a vector in a three-dimensional  $d, p, h$  space. Equation 7.8 gives the magnitude of the vector in terms of its components. A solvent, therefore, with given values of  $\delta_{p1}$ ,  $\delta_{d1}$ , and  $\delta_{h1}$  is represented as a point in space, with  $\delta$  being the vector from the origin to this point.

A polymer is also characterized by  $\delta_{p2}$ ,  $\delta_{d2}$ , and  $\delta_{h2}$ . Furthermore, it has been found on a purely empirical basis that if  $\delta_d$  is plotted on a scale twice the size as that used for  $\delta_p$  and  $\delta_h$ , then all solvents that dissolve that polymer fall within a sphere of radius  $R$  surrounding the point ( $\delta_{p2}$ ,  $\delta_{d2}$ , and  $\delta_{h2}$ ).

Solubility judgments for the determination of  $R$  are usually based on visual observation of 0.5 g polymer in 5 cm<sup>3</sup> of solvent at room temperature. Given the concentration and temperature dependence of the phase boundaries in Fig. 7.1, this is somewhat arbitrary, but it seems to work out pretty well in practice, probably because the boundaries are fairly "flat" for polymers of reasonable molecular weight.

The three-dimensional equivalent of (7.4) is obtained by calculating the magnitude of the vector from the center of the polymer sphere ( $\delta_{p2}$ ,  $\delta_{d2}$ , and  $\delta_{h2}$ ) to the point representing the solvent ( $\delta_{p1}$ ,  $\delta_{d1}$ , and  $\delta_{h1}$ ). If this is less than  $R$ , the polymer is deemed soluble:

$$[(\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 + 4(\delta_{d1} - \delta_{d2})^2]^{1/2} < R \quad \text{for solubility} \quad (7.9)$$

(The factor of 4 arises from the empirical need to double the  $\delta_d$  scale to achieve a spherical solubility region).

Figure 7.4 shows the solubility sphere for polystyrene ( $\delta_d = 8.6$ ,  $\delta_p = 3.0$ ,  $\delta_h = 2.0$ ,  $R = 3.5$ , all in hildebrands).<sup>4</sup> Note that parts of the polystyrene sphere lie outside the first octant. The physical significance of these areas is questionable, at best.

The range of  $\delta_d$ 's spanned by typical polymers and solvents is rather small. In practice, therefore, the three-dimensional scheme is often reduced to two dimensions, with polymers and solvents represented on  $\delta_h$ - $\delta_p$  coordinates with a polymer solubility circle of radius  $R$ .

Values of the individual components  $\delta_h$ ,  $\delta_p$  and  $\delta_d$  have been developed from measured  $\delta$  values, theoretical calculations, studies on model compounds, and plenty of computer fitting. They are extensively tabulated for solvents.<sup>4-9</sup> They, along with  $R$ , are less readily available for polymers, but have been published.<sup>4,5,9</sup> Mixed solvents are handled by weighting the individual  $\delta_j$  components according to (7.5).

Despite its semiempirical nature, the three-dimensional solubility parameter has proved of great practical utility, particularly in the paint industry, where the choice of solvents to meet economic, ecological, and safety constraints is of

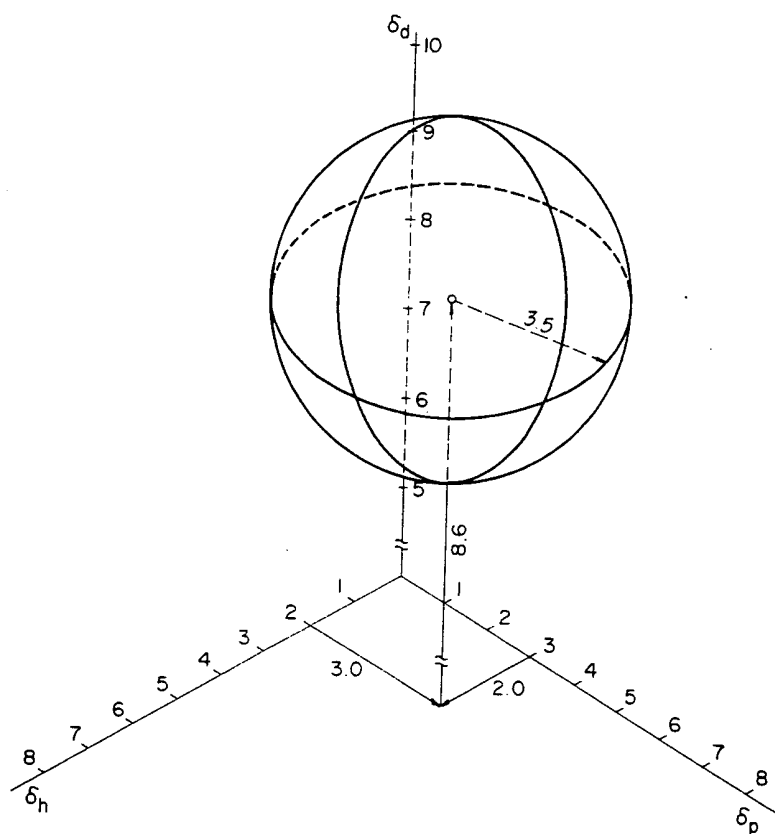


Figure 7.4 The Hansen solubility sphere for polystyrene ( $\delta_d = 8.6$ ,  $\delta_p = 3.0$ ,  $\delta_h = 2.0$ ,  $R = 3.5$ ).<sup>5</sup>

critical importance. It is capable of explaining those cases in which solvent and polymer  $\delta$ 's are almost perfectly matched, yet the polymer won't dissolve (the  $\delta$  vectors have the same magnitudes, but different directions), or where two nonsolvents can be mixed to form a solvent (the solvent components lie on opposite sides outside the sphere, the mixture within). Inorganic pigments may also be characterized by  $\delta$  vectors. Pigments whose  $\delta$  vectors closely match those of a solvent tend to form stable suspensions in that solvent.

**Example 2.** A polymer has a solubility parameter  $\delta = 9.95$  ( $\delta_p = 7.0$ ,  $\delta_d = 5.0$ ,  $\delta_h = 5.0$ ) and a solubility sphere of radius  $R = 3.0$  (all numbers in hildebrands). Will a solvent with  $\delta = 10$  ( $\delta_p = 8$ ,  $\delta_d = 6$ ,  $\delta_h = 0$ ) dissolve it?

**Solution.** No. The solvent point lies in the  $\delta_p$ - $\delta_d$  plane (i.e.,  $\delta_h = 0$ ). The closest approach the polymer solubility sphere makes to this plane is  $5.0 - 3.0 = 2$ . Thus, despite nearly identical  $\delta$ 's, the solvent will not dissolve the polymer.

## 7.7 THE FLORY-HUGGINS THEORY

Theoretical treatment of polymer solutions is essentially similar to the Huggins theory. For low molecular weight molecules have the polymeric component corresponds to the same volume fraction.

By statistical mechanics, Flory and Huggins entropy change for  $n_1$  moles of solvent is

where the  $\phi$ 's are

and the  $x$ 's are solvent,  $x_1 = 1$  must be included. usually taken as error. (Writing segmental volume and  $b$ ,  $n_2 = 20$  polymeric solvent)

### Example 3.

- 500 g of solvent
- 500 g of solvent
- 500 g of solvent (PPO) (see Ch. 7 examples where another.)

**Solution.** For polymers, we generally assume that the

## 7.7 THE FLORY-HUGGINS THEORY

Theoretical treatment of polymer solutions was initiated independently and essentially simultaneously by Flory<sup>10</sup> and Huggins<sup>11</sup> in 1942. The *Flory-Huggins theory* is based on the lattice model shown in Fig. 7.2. In the case of the low molecular weight solute, Fig. 7.2a, it is assumed that the solute and solvent molecules have roughly the same volumes; each occupies one lattice site. With the polymeric solute, Fig. 7.2b, a *segment* of the polymer molecule (which corresponds roughly but not necessarily exactly to a repeating unit) has the same volume as a solvent molecule and also occupies one lattice site.

By statistically evaluating the number of arrangements possible on the lattice, Flory and Huggins obtained an expression for the (extensive) configurational entropy change (that due to geometry alone),  $\Delta S^*$ , in forming a solution from  $n_1$  moles of solvent and  $n_2$  moles of solute:

$$\Delta S^* = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (7.10)$$

where the  $\phi$ 's are volume fractions,

$$\phi_1 = \frac{x_1 n_1}{x_1 n_1 + x_2 n_2} \quad (7.10a)$$

$$\phi_2 = \frac{x_2 n_2}{x_1 n_1 + x_2 n_2} \quad (7.10b)$$

and the  $x$ 's are the number of segments in the species. For the usual monomeric solvent,  $x_1 = 1$ . For a polydisperse polymeric solute, strictly speaking, a term must be included in (7.10) for each individual species in the distribution, but  $x_2$  is usually taken as  $\bar{x}_n$ , the number-average degree of polymerization, with little error. (Writing the volume fractions in terms of moles implies equal molar segmental volumes.) Note that while  $\phi_1$ ,  $\phi_2$ , and  $n_1$  are the same in Figs. 7.2a and b,  $n_2 = 20$  molecules for the monomeric solute, but only 1 molecule for the polymeric solute.

**Example 3.** Estimate the configurational entropy changes that occur when

a. 500 g of toluene (T) are mixed with 500 g of styrene monomer (S)

b. 500 g of toluene are mixed with 500 g of polystyrene (PS),  $\bar{M}_n = 100,000$

c. 500 g of PS,  $\bar{M}_n = 100,000$  are mixed with 500 g of polyphenylene oxide (PPO) (see Chapter II, Example 4K),  $\bar{M}_n = 100,000$ . (This is one of the rare examples where two high molecular weight polymers are soluble in one another.)

**Solution.**  $M_T = 92$ ,  $M_S = 104$ . Using these values and those given for the polymers, we get  $n_i = 500 \text{ g}/M_i$ . In the absence of other information, we must assume that the number of segments equals the number of repeating units for



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$\delta = 7.0$ ,  $\delta_d = 5.0$ ,  
Hildebrands).

$\delta_h = 0$ ). The  
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the polymers. Therefore,  $x_i = \bar{M}_{ni}/m_i$ , where  $m_i$  is the molecular weight of the repeating unit.  $m_{PS} = 104$ ,  $m_{PPO} = 120$ . These quantities may now be inserted in Eqs. 7.10 and 7.10a and b. The results are summarized below ( $R = 1.99 \text{ cal/mol}\cdot\text{K}$ ):

<i>i</i>	$n_i(\text{mol})$	$x_i$	$\phi_i$
a. Toluene	5.44	1	0.531
Styrene	4.81	1	0.469
$\Delta S^* = 14.1 \text{ cal/K}$			
b. Toluene	5.44	1	0.531
PS	0.005	962	0.469
$\Delta S^* = 6.85 \text{ cal/K}$			
c. PS	0.005	962	0.536
PPO	0.005	833	0.464
$\Delta S^* = 0.0138 \text{ cal/K}$			

The result for (c) illustrates why polymer-polymer solubility essentially requires a negative  $\Delta H$ .

An expression for the (extensive) enthalpy of mixing,  $\Delta H$ , was obtained by considering the change in adjacent-neighbor (molecules or segments) interactions on the lattice, specifically the replacement of [1,1] and [2,2] interactions with [1,2] interactions upon mixing:

$$\Delta H = RT\chi\phi_2n_1x_1 \quad [=] \text{ cal} \quad (7.11)$$

where  $\chi$  is the *Flory-Huggins interaction parameter*. Initially,  $\chi$  was interpreted as the enthalpy of interaction per mole of solvent divided by  $RT$ . By equating (7.2) and (7.11) (keeping in mind that the enthalpy in (7.2) is based on a unit volume of solution, while that in (7.11) is an extensive quantity) and making use of (7.10a), it may be shown that the Flory-Huggins parameter and solubility parameters are related by

$$\chi = \frac{v(\delta_1 - \delta_2)^2}{RT} \quad (7.12)$$

where  $v$  is the molar segmental volume of species 1 and 2 (assumed to be the same). For the dissolution of a polymer in a monomeric solvent,  $v$  is taken as the molar volume of the solvent,  $v_1$ . From our knowledge of solubility parameters, we see that (7.12) predicts  $\chi \geq 0$ . Actually, negative values have been observed.

If it is assumed that the entropy of solution is entirely configurational, substitution of (7.10) and (7.11) into (7.1) gives

$$\Delta G = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi\phi_2n_1x_1) \quad (7.13)$$

Again, for the middle term in the solute species suffices.

In terms of a high molecule

It is now recognized contribution to  $\chi$  is now considered of solvent division represent the contribution to the interaction

The Flory-Huggins equilibria in polymer-lower phase behavior quantitative fit to  $n_1$  (keeping potential of the and also makes scope of this polymer solution

The limitation time. It can't  $\chi$  depends on concentration theory. These volume change not valid for very considerable solubility lattice-type theory

Experiment mer-solvent solution.<sup>8</sup> They may

## 7.8 A PROM

In 1975, Abraham energy of mixing contains two parameters of extended con-

Again, for the usual monomeric solvent,  $x_1 = 1$ . For a polydisperse solute, the middle term in the right side of (7.13) must be replaced by a summation over all the solute species; however, treatment as a single solute with  $x_2 = \bar{x}_n$  usually suffices.

In terms of the Flory-Huggins theory, the criterion for complete solubility of a high molecular weight polymer across the composition range is

$$\chi \leq 0.5 \quad \text{for solubility} \quad (7.14)$$

It is now recognized that there is an interactive as well as a configurational contribution to the entropy of solution. That is also included in the  $\chi$  term, so  $\chi$  is now considered to be a  $\Delta G$  (rather than strictly a  $\Delta H$ ) of interaction per mole of solvent divided by  $RT$ . The first two terms on the right of (7.13) therefore represent the configurational entropy contribution to  $\Delta G$ , while the third term is the interaction contribution and includes both enthalpy and entropy effects.

The Flory-Huggins theory has been used extensively to describe phase equilibria in polymer systems. It can, for example, qualitatively describe the lower phase boundary (UCST) in Fig. 7.1, though it rarely gives a good quantitative fit of experimental data. Partial differentiation of (7.13) with respect to  $n_1$  (keeping in mind that  $\phi_1$  and  $\phi_2$  are functions of  $n_1$ ) gives the chemical potential of the solvent. This is, of course, a key quantity in phase equilibrium, and also makes  $\chi$  experimentally accessible. Further development is beyond the scope of this chapter, but the subject is well treated in standard works on polymer solutions.<sup>12-15</sup>

The limitations of the Flory-Huggins theory have been recognized for a long time. It can't predict an LCST (Fig. 7.1). It is perhaps not surprising that  $\chi$  depends on temperature, but it unfortunately turns out to be a function of concentration and molecular weight as well, limiting practical application of the theory. These deficiencies are thought to arise because the theory assumes no volume change upon mixing and the statistical analysis on which it is based is not valid for very dilute solutions, particularly in poor solvents. There has been considerable subsequent work done to correct these deficiencies and extend lattice-type theories.<sup>16,17</sup>

Experimental values for  $\chi$  have been tabulated for a number of polymer-solvent systems, both single values<sup>9</sup> and even as a function of composition.<sup>8</sup> They may be used with (7.14) to predict solubility.

## 7.8 A PROMISING RECENT APPROACH

In 1975, Abrams and Prausnitz<sup>18</sup> published a new equation for the Gibbs-free energy of mixtures which they called UNIQUAC (universal quasi-chemical). It contains two interaction parameters per binary pair in the mixture and two parameters characteristic of each component. The utility of UNIQUAC was extended considerably with the development of UNIFAC (UNIQUAC func-



# TEXTBOOK OF POLYMER SCIENCE

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THIRD EDITION

KOREAN STUDENT EDITION

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## PREFACE

*"I am inclined to think that the chemistry has done much to be a totally different field of electronics polymers again."†*

And indeed on the heart, polymers to new uses and improved education in the field unchanged. Some edition of this book

The present revision as a textbook. To before describing the feel has pedagogical teaching polymer science of Technology, a section on Discussion

The second edition contains up-to-date contents. I have been successful in the maturity of certain inserted in every polymerization reaction in Chapter 7, and

†Lord Todd, president of the Royal Society, in answer to the question: "What is the role of the polymer society?"

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The absence of solubility does not imply crosslinking, however. Other features may give rise to sufficiently high intermolecular forces to prevent solubility. The presence of crystallinity is the common example. Many crystalline polymers, particularly nonpolar ones, do not dissolve except at temperatures near their crystalline melting points. Because crystallinity decreases as the melting point is approached (Chapter 10) and the melting point is itself depressed by the presence of the solvent, solubility can often be achieved at temperatures significantly below the melting point. Thus linear polyethylene, with crystalline melting point  $T_m = 135^\circ\text{C}$ , is soluble in many liquids at temperatures above  $100^\circ\text{C}$ , while even polytetrafluoroethylene,  $T_m = 325^\circ\text{C}$ , is soluble in some of the few liquids that exist above  $300^\circ\text{C}$ . More polar crystalline polymers, such as 66-nylon,  $T_m = 265^\circ\text{C}$ , can dissolve at room temperature in solvents that interact strongly with them (for example, to form hydrogen bonds).

There is little quantitative information about the influence of branching on solubility; in general, branched species appear to be more readily soluble than their linear counterparts of the same chemical type and molecular weight.

Of all these systems, the theory of solubility, based on the thermodynamics of polymer solutions, is highly developed only for linear polymers in the absence of crystallinity. This theory is described in Sections C and D. Here the chemical nature of the polymer is by far the most important determinant of solubility, as is elucidated in the remainder of this section. The influence of molecular weight (within the polymer range) is far less, but it is of great importance to fractionation processes (Sections D and E), which yield information about the distribution of molecular weights in polymer samples.

**Solubility Parameters.** Solubility occurs when the free energy of mixing

$$\Delta G = \Delta H - T\Delta S$$

is negative. It was long thought that the entropy of mixing  $\Delta S$  was always positive, and therefore the sign of  $\Delta G$  was determined by the sign and magnitude of the heat of mixing  $\Delta H$ . For reasonably nonpolar molecules and in the absence of hydrogen bonding,  $\Delta H$  is positive and was assumed to be the same as that derived for the mixing of small molecules. For this case, the heat of mixing per unit volume can be approximated (Hildebrand 1950) as

$$\Delta H = v_1 v_2 (\delta_1 - \delta_2)^2$$

where  $v$  is volume fraction and subscripts 1 and 2 refer to solvent and polymer, respectively. The quantity  $\delta^2$  is the cohesive energy density or, for small molecules, the energy of vaporization per unit volume. The quantity  $\delta$  is known as the *solubility parameter*. (This expression for the heat of mixing is one of several alternatives used in theories of the thermodynamics of polymer solutions; in Section C,  $\Delta H$  is written in a different but equivalent way.)

The value of the solubility-parameter approach is that  $\delta$  can be calculated for both polymer and solvent. As a first approximation, and in the absence of strong

## CRITERIA FOR POLYMER SOLUBILITY

interactions such as hydrogen bonding, solubility can be expected if  $\delta_1 - \delta_2$  is less than 3.5–4.0, but not if it is appreciably larger.

This approach to polymer solubility, pioneered by Burrell (1955), has been extensively used, particularly in the paint industry. A few typical values of  $\delta_1$  and  $\delta_2$  are given in Table 7-1; for polymers, they are the square roots of the cohesive-energy densities of Table 1-4. Extensive tabulations have been published (Burrell 1975, Hoy 1970). Perhaps the easiest way to determine  $\delta_2$  for a polymer of known structure is by the use of the molar-attraction constants  $E$  of Table 7-2,

$$\delta_2 = \frac{\rho \sum E}{M}$$

where values of  $E$  are summed over the structural configuration of the repeating unit in the polymer chain, with repeat molecular weight  $M$  and density  $\rho$ .

The original solubility-parameter approach was developed for nonpolar systems. Modifications to include polarity and hydrogen bonding have led to three-dimensional solubility-parameter schemes, which lack the simplicity of the single-parameter method but are more widely applicable. Despite its shortcomings, the concept is nevertheless still extremely useful and should not be abandoned without test.

In contrast to the above considerations of the thermodynamics of dissolution of polymers, the rate of this step depends primarily on how rapidly the polymer and the solvent diffuse into one another (Ueberreiter 1962, Asmussen 1962). Solvents that promote rapid solubility are usually small, compact molecules, but these kinetically good solvents need not be thermodynamically good as well. Mixtures of a kinetically good and a thermodynamically good liquid are often very powerful and rapid polymer solvents.

TABLE 7-1. Typical Values of the Solubility Parameter  $\delta$  for Some Common Polymers and Solvents\*

Solvent	$\delta_1 [(\text{J}/\text{cm}^3)^{1/2}]$	Polymer	$\delta_2 [(\text{J}/\text{cm}^3)^{1/2}]$
n-Hexane	14.8	Polytetrafluoroethylene	12.7
Carbon tetrachloride	17.6	Poly(dimethyl siloxane)	14.9
Toluene	18.3	Polyethylene	16.2
2-Butanone	18.5	Polypropylene	16.6
Benzene	18.7	Polybutadiene	17.6
Cyclohexanone	19.0	Polystyrene	17.6
Styrene	19.0	Poly(methyl methacrylate)	18.6
Chlorobenzene	19.4	Poly(vinyl chloride)	19.4
Acetone	19.9	Poly(vinyl acetate)	21.7
Tetrahydrofuran	20.3	Poly(ethylene terephthalate)	21.9
Methanol	29.7	66-Nylon	27.8
Water	47.9	Polyacrylonitrile	31.5

\*Collins (1973).



TABLE 7-2. Molar Attraction Constants  $E^a$ 

Group	$E$ [(J-cm <sup>3</sup> ) <sup>1/2</sup> /mole]	Group	$E$ [(J-cm <sup>3</sup> ) <sup>1/2</sup> /mole]
-CH <sub>3</sub>	303	NH <sub>2</sub>	463
-CH <sub>2</sub> -	269	-NH-	368
>CH-	176	-N-	125
>C<	65	C≡N	725
CH <sub>2</sub> =	259	NCO	733
-CH=	249	-S-	429
>C=	173	Cl <sub>1</sub>	701
-CH=aromatic	239	Cl primary	419
>C=aromatic	200	Cl secondary	425
-O-ether, acetal	235	Cl aromatic	329
-O-epoxide	360	F	84
-COO-	668	Conjugation	47
>C=O	538	cis	-14
-CHO	599	trans	-28
(CO) <sub>2</sub> O	1159	Six-membered ring	-48
-OH→	462	ortho	-19
OH aromatic	350	meta	-13
-H acidic dimer	-103	para	-82

<sup>a</sup>Hoy (1970).

## GENERAL REFERENCES

Hildebrand 1950; Gardon 1965; Hoy 1970; ASTM D3132; Burrell 1975; Morawetz 1975, Chapter 2; Olabisi 1979, Chapter 2.3; Snyder 1980.

## B. CONFORMATIONS OF DISSOLVED POLYMER CHAINS

As specified in Chapter 1, those arrangements of the polymer chain differing by reason of rotations about single bonds are termed *conformations*.<sup>†</sup> In solution, a polymer molecule is a randomly coiling mass most of whose conformations occupy many times the volume of its segments alone. The average density of segments within a dissolved polymer molecule is of the order of  $10^{-4}$ – $10^{-5}$  g/cm<sup>3</sup>. The size of the molecular coil is very much influenced by the polymer-solvent interaction forces. In a thermodynamically "good" solvent, where polymer-solvent contacts

<sup>†</sup> Here we differ from some authorities, notably Flory (1969), who prefers the use, well established in statistical mechanics, of the term *configuration* here. We follow the convention of organic chemistry in which configuration designates stereochemical arrangement (see Chapter 10A).

## CONFORMATIONS OF DISSOLVED POLYMER CHAINS

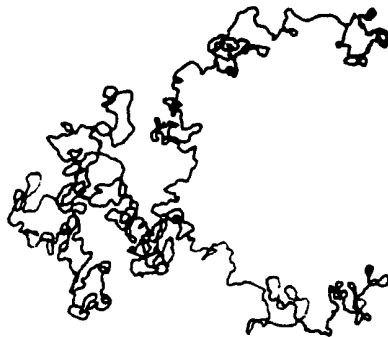


FIG. 7-1. Model of one of the many conformations of a random-coil chain of 1000 links (Treloar 1958).

are highly favored, the coils are relatively extended. In a "poor" solvent they are relatively contracted. It is the purpose of this section to describe the conformational properties of both ideal and real polymer chains. The conformations of polymer chains in the crystalline state are considered in Chapter 10B.

The importance of the random-coil nature of the dissolved, molten, amorphous, and glassy states of high polymers cannot be overemphasized. As the following chapters show, many important physical as well as thermodynamic properties of high polymers result from this characteristic structural feature. The random coil (Fig. 7-1) arises from the relative freedom of rotation associated with the chain bonds of most polymers and the formidably large number of conformations accessible to the molecule.

One of these conformations, the fully extended chain (often an all-trans planar zigzag carbon chain; Fig. 7-2), has special interest because its length, the *contour length* of the chain, can be calculated in a straightforward way. In all other cases the size of the random coil must be expressed in terms of statistical parameters such as the root-mean-square distance between its ends,  $(\bar{r}^2)^{1/2}$ , or its *radius of gyration*, the root-mean-square distance of the elements of the chain from its center of gravity,  $(\bar{s}^2)^{1/2}$ . For linear polymers that are not appreciably extended beyond their most probable shape, the mean-square end-to-end distance and the square of the radius of gyration are simply related:  $\bar{r}^2 = 6\bar{s}^2$ . For extended chains  $\bar{r}^2 > 6\bar{s}^2$ . The use of the radius of gyration is sometimes preferred because it can be determined experimentally, as described in Chapter 8E.

**The Freely Jointed Chain.** A simple model of a polymer chain consists of a series of  $x$  links of length  $l$  joined in a linear sequence with no restrictions on the angles between successive bonds. The probability  $W$  that such an array has a given end-to-end distance  $r$  can be calculated by the classical random-flight method (Ray-

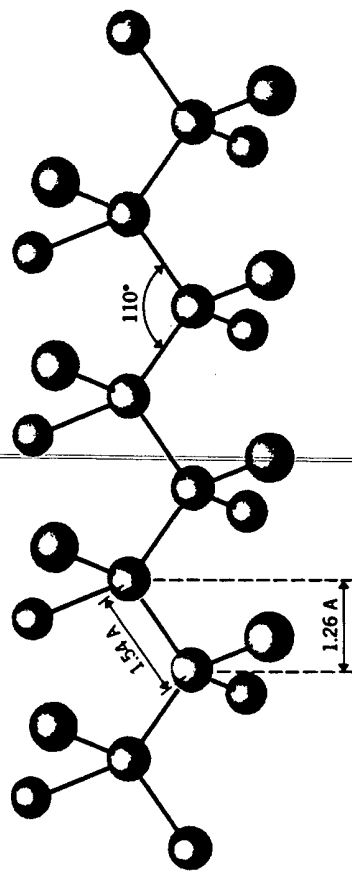


FIG. 7-2. The fully extended all-trans conformation of the carbon-carbon chain (Billmeyer 1969).

leigh 1919). The most important result of the calculation is that the end-to-end distance is proportional to the square root of the number of links:

$$(\bar{r}^2)^{1/2} = Lx^{1/2}$$

(The subscript  $f$  indicates the random-flight end-to-end distance.) Thus  $(\bar{r}^2)^{1/2}$  is proportional to  $M^{1/2}$ , or  $\bar{r}^2/M$  is a characteristic property of the polymer chain structure, independent of molecular weight or length.

The distribution of end-to-end distances over the space coordinates  $W(x, y, z)$  is given by the Gaussian distribution function shown graphically in Fig. 7-3. This is the density distribution of end points and shows that if one end of the chain is taken at the origin, the probability is highest of finding the other end in a unit volume

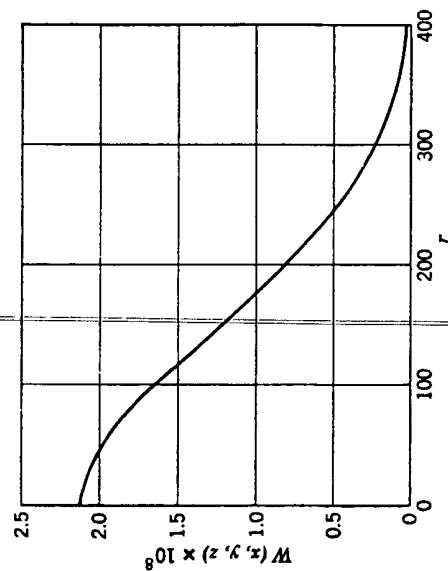


FIG. 7-3. Gaussian distribution of end-to-end distances in a random coil of  $10^4$  links each 2.5 Å long;  $W(x, y, z)$  is expressed in angstroms to the inverse third power and  $r$  in angstroms.

## CONFORMATIONS OF DISSOLVED POLYMER CHAINS

near the origin. This probability decreases continuously with increasing distance from the origin. On the other hand, the probability of finding a chain end within the volume of a spherical shell between distances  $r$  and  $r + dr$  from the origin has a maximum, as shown in Fig. 7-4. It should be noted that the Gaussian distribution does not fall to zero at large extensions and so must fail to describe the actual conformations of the chain where  $r$  nears the contour length. Over most of the range of interest for the dilute-solution properties of polymers, this is of little consequence; better approximations are available where needed, as in the treatment of rubber elasticity (Chapter 11B).

The freely jointed or random-flight model seriously underestimates the true dimensions of real polymer molecules for two reasons: First, restrictions to completely free rotation, such as fixed valence angles, the correct weights for trans and gauche conformations, and statistical deviations from ideal trans and gauche states, and other short-range interactions described below, lead to larger dimensions than calculated above; and second, long-range interactions resulting from the inability of chain atoms far removed from one another to occupy the same space at the same time result in a similar effect.

**Short-Range Interactions.** One of the triumphs of modern polymer chemistry is the extent to which Flory and his collaborators (Flory 1969), among others, have calculated completely and accurately the effect of short-range interactions on the dimensions of random-coil polymers. Several effects are involved. The restriction to fixed bond angle  $\theta$  expands the chain by a factor of  $[(1 - \cos \theta)/(1 + \cos \theta)]^{1/2}$ , equal to  $\sqrt{2.0}$  for carbon-carbon bonds. Restricted rotation, whether resulting from steric hindrances and resulting potential-energy barriers or from resonance leading to rigid planar conformations, increases dimensions still more. Finally, conformations that would place two atoms close together along the chain too close to one another are not allowed, leading to further expansion. The most important of these is the so-called *pentane interference* (Taylor 1948) between the first and fifth chain atoms in a sequence. Bovey (1979) summarizes these conformational features.

The net results of these short-range interactions can be expressed as a *charac-*

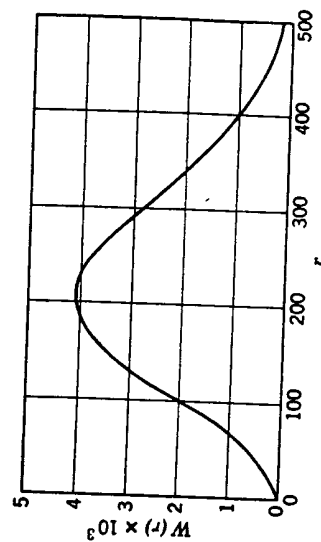


FIG. 7-4. Radial distribution of end-to-end distances for the coil of Fig. 7-3. Here  $W(r)$  is expressed in angstrom<sup>-1</sup> units.

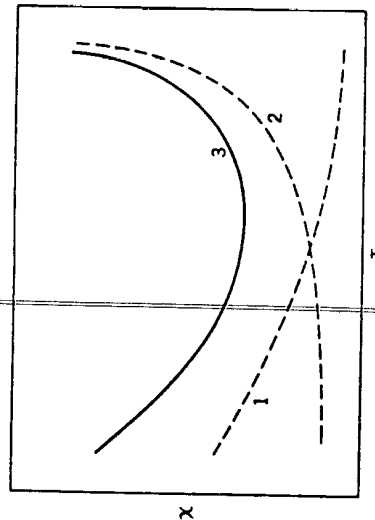


FIG. 7-8. Qualitative behavior of the parameter  $\chi_1$  according to the corresponding-state theories: curve 1, contribution from enthalpic polymer-solvent interactions (as predicted by the Flory-Huggins theory); curve 2, contribution due to free-volume dissimilarity between polymer and solvent; curve 3, total  $\chi_1$ , sum of 1 and 2 (Patterson 1969).

## GENERAL REFERENCES

Flory 1953; Huggins 1958; Carpenter 1970; Tager 1978; de Gennes 1979, Chapter 3; Kwei 1979, Chapter 4.2.

## D. PHASE EQUILIBRIUM IN POLYMER SOLUTIONS

### Polymer-Solvent Miscibility

This section is concerned with the equilibrium between two liquid phases, both of which contain amorphous polymer and one or more solvents. The treatment of cases involving a crystalline polymer phase is more complex and is given in part in Section E and in part in Chapter 10C.

When the temperature of a polymer solution is raised or lowered, the solvent eventually becomes thermodynamically poorer. Finally a temperature is reached beyond which polymer and solvent are no longer miscible in all proportions. At more extreme temperatures the mixture separates into two phases. Such phase separation may also be brought about by adding a nonsolvent liquid to the solution. In either case it takes place when the interaction parameter  $\chi_1$  exceeds a critical value near  $\frac{1}{2}$  (see below).

It was shown in Section C that the Flory-Huggins theory attributes  $\chi_1$  to polymer-solvent interactions alone, and predicts it to increase monotonically as the temperature decreases (Fig. 7-8). Thus phase separation is predicted to take place only on lowering the temperature, the phase diagram looking like that in the lower portion of Fig. 7-9. The maximum temperature for phase separation is designated the *upper critical solution temperature*. Although it was not frequently observed

## PHASE EQUILIBRIUM IN POLYMER SOLUTIONS

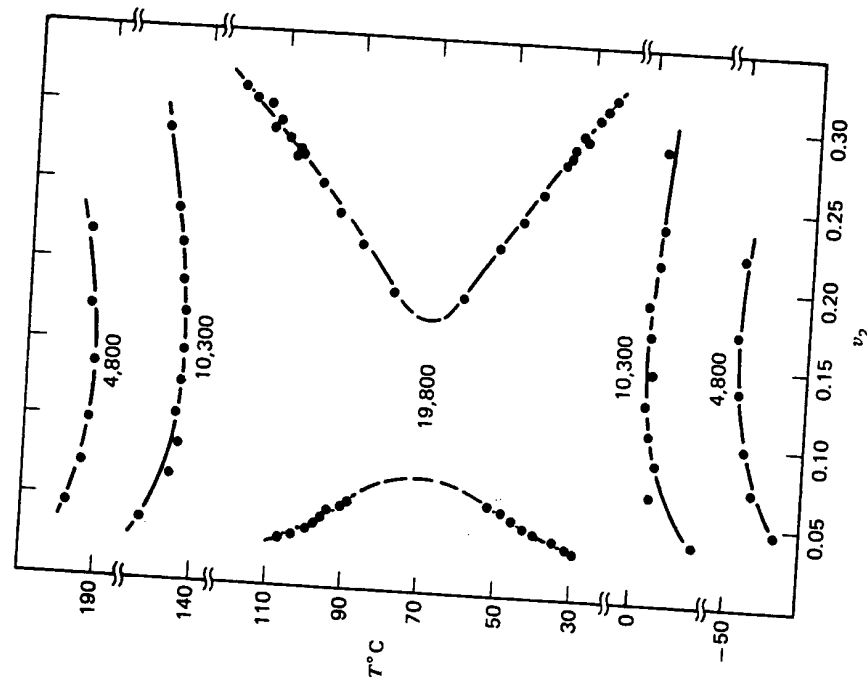


FIG. 7-9. Phase diagram of the system polystyrene in acetone, showing phase separation at upper and lower critical solution temperatures for polymer of the molecular weights indicated. Reprinted with permission from Siow 1972. Copyright 1972 by the American Chemical Society.)

until recent years (Freeman 1960), it is now recognized that phase separation invariably occurs also when the temperature is raised until a *lower critical solution temperature*<sup>†</sup> (Fig. 7-9, upper area) is reached. This phenomenon is explained by the corresponding-state theories of polymer solutions described qualitatively in Section C. The contribution to  $\chi_1$  from the free-volume dissimilarity between polymer and solvent is an increasing function of the temperature (Fig. 7-8). The total interaction parameter thus goes through a minimum, and two critical values of  $\chi_1$  are accessible. Each has the character of a  $\Theta$  temperature (see below); at each the

<sup>†</sup>The perverse names of the upper and lower critical solution temperatures relate more directly to an alternative case (the common example is nicotine in water) in which the upper critical solution temperature is higher than the lower one and the phase diagram consists of a region of immiscibility completely surrounded by a one-phase region.

second virial coefficient approaches zero and the polymer chain approaches its unperturbed dimensions.

For the remainder of this section reference is made only to phase separation at an upper critical solution temperature. The predictions of the Flory-Huggins theory remain unchanged except for the sign of the temperature dependence in the case of a lower critical solution temperature.

#### Binary Polymer-Solvent Systems.

The condition for equilibrium between two phases in a binary system is that the partial molar free energy of each component be equal in each phase. This condition corresponds to the requirement that the first and second derivatives of  $\Delta\bar{G}_1$  (Eq. 7-10) with respect to  $v_2$  be zero. Application of this condition leads to the critical concentration at which phase separation first appears:

$$v_{2c} = \frac{1}{1 + x^{1/2}} \approx \frac{1}{x^{1/2}} \quad (7-22)$$

This is a rather small volume fraction; for a typical polymer ( $x \approx 10^4$ ),  $v_{2c} \approx 0.01$ . The critical value of  $\chi_1$  is given by

$$\chi_{1c} = \frac{(1 + x^{1/2})^2}{2x} \approx \frac{1}{2} + \frac{1}{x^{1/2}} \quad (7-23)$$

The critical value of  $\chi_1$  exceeds  $\frac{1}{2}$  by a small increment, depending on molecular weight, and at infinite molecular weight equals  $\frac{1}{2}$ . The temperature at which phase separation begins is given by

$$\frac{1}{T_c} = \frac{1}{\Theta} \left[ 1 + \frac{1}{\psi_1} \left( \frac{1}{x^{1/2}} + \frac{1}{2x} \right) \right] \approx \frac{1}{\Theta} \left( 1 + \frac{C}{M^{1/2}} \right) \quad (7-24)$$

where  $C$  is a constant for the polymer-solvent system. Thus  $1/T_c$  (K) varies linearly with the reciprocal square root of molecular weight. The Flory temperature  $\Theta$  is the critical miscibility temperature in the limit of infinite molecular weight.

The qualitative features of the theory are in agreement with experiment. The dependence of precipitation temperature on polymer concentration is shown in Fig. 7-10. The critical values  $T_c$  and  $v_{2c}$  correspond to the maxima in the curves. In the neighborhood of the critical point the polymer concentration in the dilute phase is extremely small. The phenomenon of the coexistence of two liquid phases, one of which is a dilute solution and the other nearly pure solvent, is called *coacervation* (Section E).

The discrepancy between theory and experiment results (Koningsveld 1968) from the effect of finite molecular-weight distribution breadth in the polymer samples used.

#### PHASE EQUILIBRIUM IN POLYMER SOLUTIONS

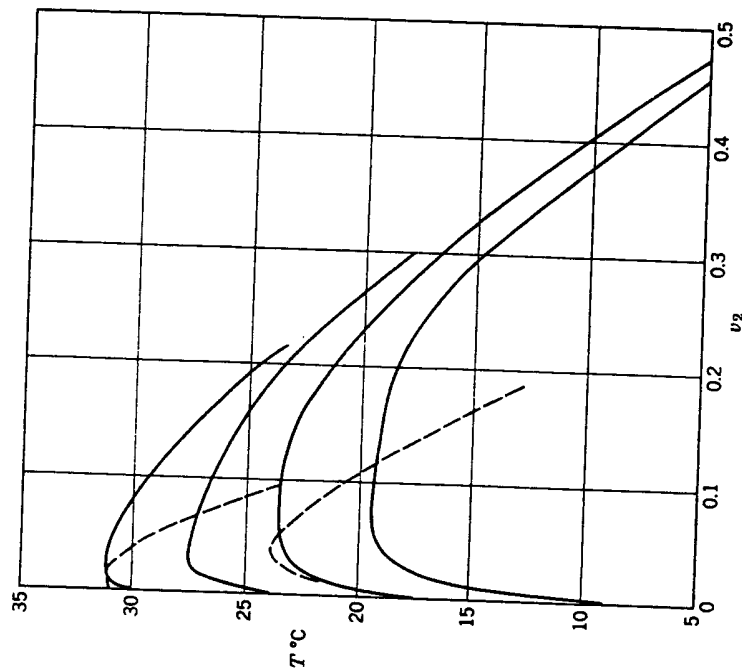


FIG. 7-10. Phase diagram showing precipitation temperature as a function of polymer concentration for fractions of polystyrene in diisobutyl ketone (Shultz 1952). Higher-molecular-weight fractions precipitate at higher temperatures (solid lines, experimental; dotted lines, theoretical).

The dependence of  $T_c$  upon molecular weight is shown in Fig. 7-11. The curves are accurately linear, and the Flory temperatures  $\Theta$  obtained from the intercepts agree within experimental error ( $<1^\circ$ ) with those derived from osmotic measurements, taking  $\Theta$  to be the temperature where  $A_2$  is zero. Precipitation measurements on a series of sharp fractions offer perhaps the best method of determining  $\Theta$ .

**Ternary Systems.** Although a thorough discussion of ternary systems is outside the scope of this book, a few cases have particular interest. The most commonly encountered system is that of polymer, solvent, and nonsolvent. The phase relations are conveniently displayed in the usual ternary diagram (Fig. 7-12). The position of the *binodal curve*, along which two phases are in equilibrium, depends upon molecular weight; the limiting critical point at infinite molecular weight is the analog of  $\Theta$  in a two-component system.

**Multicomponent Systems.** The theory of phase separation in systems comprising a heterogeneous polymer in a single solvent is developed with the simplifying assumption that the interaction constants  $\chi$  for all values of  $x$  are identical; only

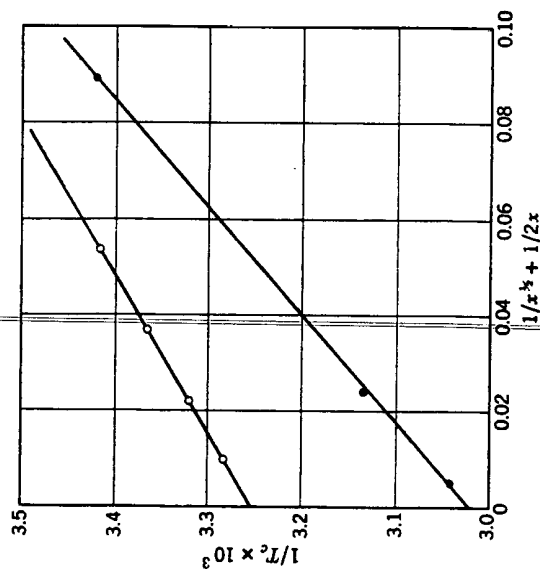


FIG. 7-11. Dependence of critical temperature for phase separation on molecular weight for (O) polystyrene in cyclohexane, and (●) polyisobutylene in diisobutyl ketone (Shultz 1952).

the size parameter  $x$  itself varies from one molecular species to another. In theory, all details of the system could be calculated from a knowledge of the size distribution of the polymer and the equilibrium conditions. In practice, this would be an enormous task; but the principal point of interest, namely, the efficiency with which molecular species are separated between the two phases, is simply derived. It is given by the equation

$$\ln \left( \frac{v'_x}{v_x} \right) = \sigma x \quad (7-25)$$

where  $v'_x$  and  $v_x$  are, respectively, the concentrations of species  $x$  in the precipitated or more concentrated phase (primed) and the dilute phase (unprimed), and

$$\sigma = v_2 \left( 1 - \frac{1}{\bar{x}_n} \right) - v_2' \left( 1 - \frac{1}{\bar{x}_n} \right) + \chi_1 [(1 - v_2)^2 - (1 - v_2')^2] \quad (7-26)$$

Here  $v'_2$  and  $v_2$  are the total polymer concentrations in the two phases, and  $\bar{x}_n$  is the number average of  $x$ . The parameter  $\sigma$  thus depends in a complicated way on the relative amounts of all the polymer species in each phase. The following conclusions may be drawn from the theory:

- A part of any given polymer species is always present in each phase. In fact, every species is actually more soluble in the precipitated phase, that is,  $v'_x > v_x$  for all values of  $x$ .

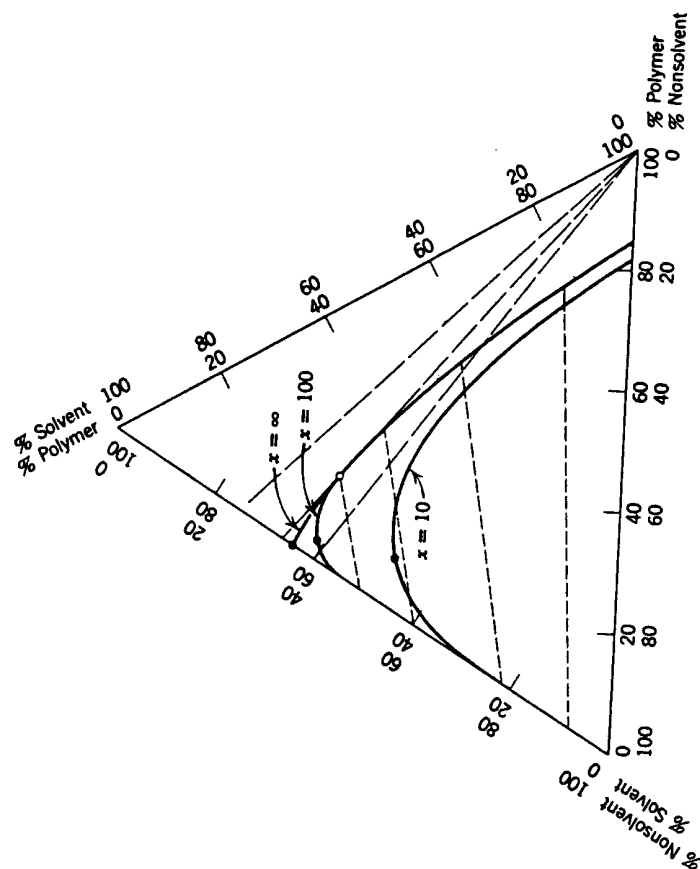


FIG. 7-12. Ternary phase diagram for a polymer-solvent-nonsolvent system, showing phase separation boundaries for the indicated values of  $x$ . Dotted lines are tie lines for  $x = 100$ , connecting points representing the compositions of pairs of phases in equilibrium. Dashed lines represent constant solvent-nonsolvent ratios (O, critical points; O, precipitation threshold for  $x = 100$ ).

- Since  $\sigma$  depends on the concentrations of all species and on the details of their weight distribution, the result of a fractionation cannot be predicted in advance unless the details of the distribution are known. The Flory-Huggins theory predicts that only the number average  $\bar{x}_n$  for each phase appears in  $\sigma$ , while an alternative analysis (Stockmayer 1949) expresses  $\sigma$  in terms of higher moments of the distribution for the whole polymer.
- Fractionation is significantly more efficient in very dilute solutions: If  $R = v'/v$ , the ratio of the volumes of the precipitated and dilute phases, the fraction  $f_x$  of the constituent  $x$  in the dilute phase is

$$f_x = \frac{1}{1 + R e^{\sigma x}} \quad (7-27)$$

and that in the precipitated phase is

$$f'_x = \frac{R e^{\sigma x}}{1 + R e^{\sigma x}} \quad (7-28)$$

## POLYMER SOLUTIONS

If  $R \ll 1$ , most of the smaller species remain in the dilute phase because of its greater volume. The larger partition factor  $u_x'/u_x$  for the higher-molecular-weight species causes them to appear selectively in the precipitated phase despite its smaller volume.

The resulting inefficient nature of the fractionation process is illustrated in Figs. 7-13 and 7-14. Figure 7-13 shows in the three lower curves the distribution of polymer species left in the dilute phase after precipitation at various values of  $R$ . The initial distribution is shown in the upper curve. The increase in efficiency as  $R$  becomes smaller is apparent. Figure 7-14 shows the overlapping distribution curves resulting even when  $R$  is unusually small. It is clear that separation into fractions that are close to monodisperse is a most difficult and time-consuming process. It should be noticed that the distribution curves of the fractions in Fig. 7-14 become narrower at lower molecular weights.

The foregoing discussion refers to fractionation by cooling from a single solvent. Similar considerations apply to fractionation at constant temperature in a solvent-nonsolvent system. A difference arises in that the solvent composition is different in the two phases. This difference should lead to more efficient fractionation in solvent-precipitant mixtures. Experimental evidence for such an effect has not been reported.

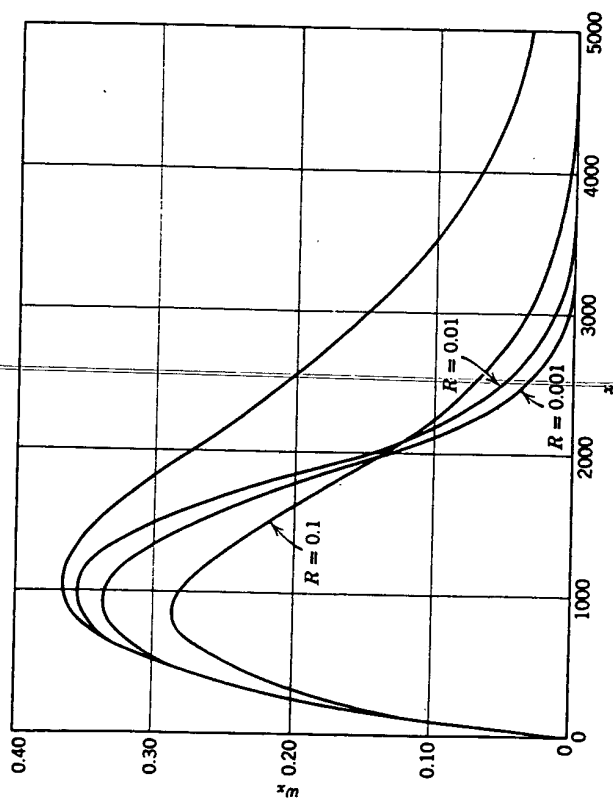


FIG. 7-13. Calculated separation of a polymer having the molecular-weight distribution shown in the upper curve with  $R = 0.1$ ,  $0.01$ , and  $0.001$ ,  $f_s$  chosen to be  $\frac{1}{2}$  at  $x = 2000$  in each case (Flory 1953).

## PHASE EQUILIBRIUM IN POLYMER SOLUTIONS

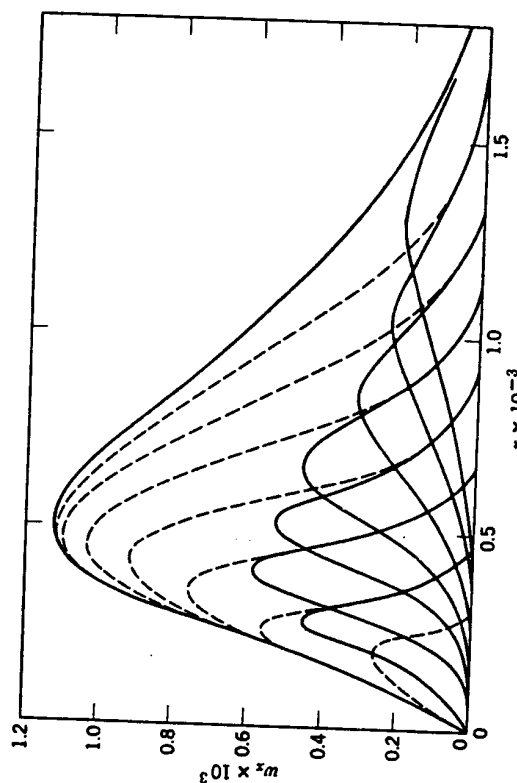


FIG. 7-14. Calculated distributions of a series of eight fractions separated from the distribution of the upper curve (Flory 1953);  $R = 0.001$  in each case. Dashed curves represent the polymer remaining in the dilute phase after each successive precipitation.

**Scaling Concepts.** Figure 7-15 shows one important result of the application of scaling concepts to polymer physics. It is a typical phase diagram of a polymer solution, with the coordinates concentration  $c$  and reduced temperature  $\tau = (T - \Theta)/\Theta$ , showing the regions in which the application of scaling concepts becomes important. The dashed curve in the negative region of  $\tau$  (region IV) is a coexistence or phase-separation curve of the type shown in Fig. 7-10. Region I' is the  $\Theta$  region, of dilute solutions near  $T = \Theta$  and  $\tau = 0$ . Region I is the dilute region, limited by a value of  $\tau$  proportional to  $(\bar{M}^2)^{-1/2}$ , and the line of  $c^*$  the critical concentration at which the chains begin to overlap;  $c^*$  is also proportional to  $(\bar{M}^2)^{-1/2}$ . Region II is the semidilute region within which chain overlap becomes more and more important. The concentration  $c^{**}$  is, as seen, proportional to  $\tau$ . Region III is the semidilute and concentrated  $\Theta$  region, not yet studied in detail.

In several of these regions the Flory-Huggins theory describes the situation adequately. The critical point for phase separation, for example, is located correctly, but the shape of the coexistence curve in that region is not properly described by that theory. The properties of the polymer-rich phase are adequately described by the Flory-Huggins theory.

## Polymer-Polymer Miscibility

Because of the commercially interesting properties of compatible polymer blends, interest in phase separation in polymer-polymer systems has increased in recent

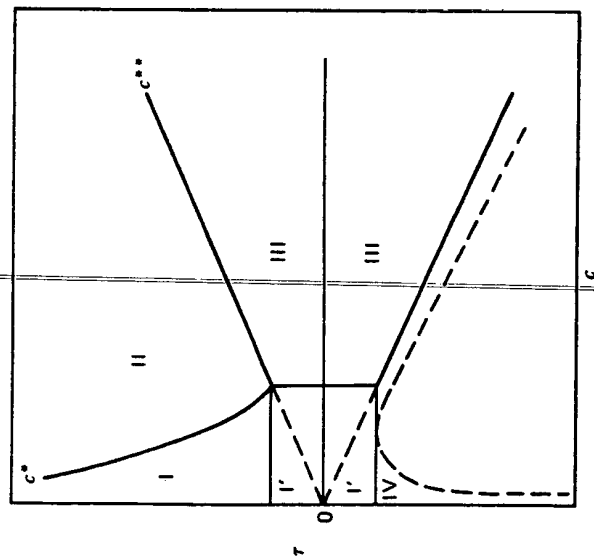


FIG. 7-15. Typical phase diagram of a polymer solution. See the text for explanation. (Reprinted with permission from Daoud 1976, Figure 3, page 974.)

years. In general, polymers mixed in pairs tend to be totally immiscible, but a significant number of exceptions exist and have been listed by Krause (1978).

Each of the several theories of polymer solution thermodynamics contributes to an understanding of polymer-polymer miscibility. Use of the solubility parameter predicts, for example, that for miscibility over the entire composition range the difference in solubility parameters of the two polymers cannot exceed 0.7 at  $M = 10,000$ , 0.2 at  $M = 100,000$ , or 0.08 at  $M = 1,000,000$ . The Flory-Huggins theory describes all the observed behavior, provided that interaction parameters are determined experimentally, but it does not provide a derivation of them, an understanding of the origin of the observed behavior, or predictive powers. The corresponding-state theory overcomes many of these limitations and leads to several conclusions at variance with the predictions of the Flory-Huggins theory.

The thermodynamics of phase separation in block copolymers has been developed by Krause (1970) and Meier (1969).

## GENERAL REFERENCES

- Flory 1953; Casassa 1977; Elias 1977, Chapter 6.6; Paul 1978; de Gennes 1979, Chapter 4; Kwei 1979, Chapter 4.3; Olabisi 1979.

## FRACTIONATION OF POLYMERS BY SOLUBILITY

### E. FRACTIONATION OF POLYMERS BY SOLUBILITY

In this section are discussed only the most important and widely practiced techniques for fractionating polymers by solubility differences. Many variations and less useful techniques exist and are reviewed by Hall (1959), Guzmán (1961), and Cantow (1967).

#### Bulk Fractionation by Nonsolvent Addition

Fractional precipitation in bulk (Kotera 1967) is carried out by adding the nonsolvent to a dilute solution of the polymer until a slight turbidity develops at the temperature of fractionation. To ensure the establishment of equilibrium the mixture may be warmed until it is homogeneous and allowed to cool slowly back to the required temperature, which should thereafter be carefully maintained. The precipitated phase is allowed to settle to a coherent layer, and the supernatant phase is removed. A further increment of precipitant is added and the process repeated. The polymer is isolated from the precipitated phase, which may still be relatively dilute (perhaps 10% polymer).

Refractionation is often used to achieve better separation. A more efficient procedure is to restrict the initial experiments to very dilute solutions, or to refine each initial fraction by a single reprecipitation at higher dilution, returning the unprecipitated polymer from this separation to the main solution before the next fraction is removed.

The solvent and the precipitant should be chosen so that precipitation occurs over a relatively wide range of solvent composition yet is complete before too high a ratio of precipitant to solvent is reached. Other important considerations are the stability and volatility of the liquids and their ability to form a highly swollen, mobile gel phase. Relatively simple equipment, for example, a three-neck flask of several liters capacity (Fig. 7-16), is adequate for bulk precipitation fractionation.

#### Column Elution

**Solvent-Gradient Elution.** In elution methods (Elliott 1967), polymer is placed in contact with a series of liquids of gradually increasing solvent power. Species of lowest molecular weight, and thus highest solubility, dissolve in the first liquid, and successively higher molecular-weight fractions in subsequent liquids. To ensure rapid equilibration, the polymer must be present as a very thin film. For convenience, the polymer is often applied to a finely divided substrate such as sand or glass beads, which is subsequently used to pack a column. By the use of mixing vessels, a continuous gradient of solvent-nonsolvent composition can be produced and eluted through the column.

**Thermal-Gradient Elution.** A modification of the solvent-gradient method utilizes a small temperature gradient from one end to the other of the column, in addition to the gradient of solvent composition (Baker 1956, Porter 1967). The



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# POLYMER HANDBOOK

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THIRD EDITION

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# Solubility Parameter Values

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where  $\Delta G_m$  = the Gibbs free energy change on mixing,  $\Delta H_m$  = the enthalpy change on mixing,  $T$  = the absolute temperature, and  $\Delta S_m$  = the entropy change on mixing. A negative  $\Delta G_m$  predicts that a process will occur spontaneously. Since the dissolution of a high-molecular-weight polymer is always connected with a large increase in entropy, the enthalpy term (the sign and magnitude of  $\Delta H_m$ ) is the deciding factor in determining the sign of the Gibbs free energy change. Solubility parameters were developed to describe the enthalpy of mixing of simple liquids (nonpolar, nonassociating solvents), but have been extended to polar solvents and polymers.

Hildebrand and Scott (59) and Scatchard (101) proposed that

$$\Delta H_m = V \left( \left( \frac{\Delta E_1^v}{V_1} \right)^{1/2} - \left( \frac{\Delta E_2^v}{V_2} \right)^{1/2} \right)^2 \phi_1 \phi_2 \quad (2)$$

where  $V$  = volume of the mixture,  $\Delta E_i^v$  = energy of vaporization of species  $i$ ,  $V_i$  = molar volume of species  $i$ , and  $\phi_i$  = volume fraction of  $i$  in the mixture.  $\Delta E_i^v$  is the energy change upon isothermal vaporization of the saturated liquid to the ideal gas state at infinite volume (94). The cohesive energy density (CED),  $\Delta E_i^v$ , is the energy of vaporization per  $\text{cm}^3$ . The solubility parameter has been defined as the square root of the cohesive energy density and describes the attractive strength between molecules of the material

$$\delta_i = \left( \frac{\Delta E_i^v}{V_i} \right)^{1/2} \quad (3)$$

The dimensions of  $\delta_i$  are  $(\text{cal}/\text{cm}^3)^{1/2} = (4.187 \text{ J}/10^{-6} \text{ m}^3)^{1/2} = 2.046 \times 10^3 (\text{J}/\text{m}^3)^{1/2} = 2.046 (\text{MPa})^{1/2}$ . The solubility parameter can be considered as the 'internal pressure' of the solvent (9-11). Equation 2 can be rewritten to give the heat of mixing per unit volume for a binary mixture

$$\frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (4)$$

In order for  $\Delta G_m$  in Eq. 1 to be less than zero, the heat of mixing must be smaller than the entropic term.  $\Delta G_m$  will always be less than zero for regular solutions if  $\delta_1 = \delta_2$  and the components will be miscible in all proportions. In general  $(\delta_1 - \delta_2)^2$  must be small for the components to be miscible. Equation 4 gives the heat of mixing of regular solutions in which the components mix with (a)

## INTRODUCTION

In this section, cohesive energy density and solubility parameters are defined and some of the limitations of solubility parameters are discussed.

### Cohesive Energy Density and the Solubility (Hildebrand) Parameter

The process of dissolving an amorphous polymer in a solvent is described by the free energy of mixing

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (1)$$

no volume change on mixing at constant pressure, (b) no reaction between the components, and (c) no complex formation or special associations (114).  $\delta_i$  of Eq. 3 is often called the Hildebrand parameter. Some researchers (13) prefer the term 'cohesion parameter' since it correlates with a large number of physical and chemical properties and not just the miscibility of components. The solubility parameter of a mixture is often taken to be the sum of the products of the component solubility parameters with their volume fractions.

$\Delta E_i^v$  is related to the enthalpy of vaporization

$$\Delta E_i^v = \Delta H_i^v - RT \quad (5)$$

where  $R$  = ideal gas constant. The solubility parameter of solvents can be determined by measuring the enthalpy of vaporization (or using a correlation for  $\Delta H_i^v$ ) and using Eq. 6.

$$\delta_i = \left( \frac{H_i^v - RT}{V_i} \right)^{1/2} \quad (6)$$

Equation 5 is a simplified description of the molar cohesive energy. A complete description is given below (95).

$$\Delta E_i^v = \Delta H_i^v + \Delta H_i^s - RT + p_s V_i \quad (7)$$

where  $\Delta H_i^s$  = molar increase in enthalpy on isothermally expanding the saturated vapor to zero pressure and  $p_s$  = saturation vapor pressure at temperature  $T$ . At pressures below 1 atm, the  $\Delta H_i^s$  and  $p_s V_i$  terms are usually much less than  $\Delta H_i^v$  and  $RT$ , and Eq. 7 reduces to Eq. 5. At the critical point,  $\Delta H_i^v = 0$  and Eq. 5 incorrectly predicts a negative value for the cohesive energy density while Eq. 7 yields a small positive value.

Equation 1 can be modified for crystalline polymer phase equilibria by including terms for the heat of fusion and the entropy change associated with the disruption of the crystal lattice. Some crystalline polymers obey the solubility parameter model at temperatures near their melting point,  $T \geq 0.9 T_m$  (123). Solvent swelling experiments with crystalline polymers may fit the model.

## 1.2 Cohesive Energy Parameters for Polar Systems

The solubility parameter describes the enthalpy change on mixing of nonpolar solvents well but does not give uniform results when extended to polar systems. Table 3.1 contains a list of a wide variety of liquids categorized by low, medium, and high hydrogen-bonding capacities (21–24). Complete miscibility is expected to occur if the solubility parameters are similar and the degree of hydrogen bonding is similar between the components. Hydrocarbons, chlorinated hydrocarbons, and nitrohydrocarbons are considered to be poor hydrogen-bonding solvents. Ketones, esters, and glycol monoethers give moderate hydrogen bonding. Alcohols, amines, acids, amides, and aldehydes are strong hydrogen bonding solvents. Tables 3.1, 3.2, and 3.4 classify materials with the designations  $p$ ,  $m$ , and  $s$  referring to these categories. Alternative classifications have been given by Lieberman (69), Gardon (41, 85, 86), and Dyck and Hoyer (32).

Other investigators have decomposed the Hildebrand parameter into several terms, representing different contributions to the energy of mixing. Hildebrand (59) used dispersive and polar solubility terms for solvents with the complete parameter given by

$$\delta^2 = \delta_d^2 + \delta_p^2 \quad (8)$$

where  $\delta_d$  = the dispersive term and  $\delta_p$  = the polar term. The additional term improved agreement between  $\delta$  and experimental data. Prausnitz and co-workers accounted for polar bonding by including parameters for permanent dipole interactions and dispersion type interactions. This approach has been applied to polymer solutions (15) and complex formation (57). Crowley et al. (26, 27) proposed a three-parameter system.

Hansen (49–53, 56) and Hansen and Skaarup (54) assume that the cohesive energy arises from dispersive, permanent dipole-dipole interactions and hydrogen bonding forces

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (9)$$

where  $\delta_d$  = dispersive term,  $\delta_p$  = polar term, and  $\delta_h$  = hydrogen bonding term.  $\delta_h$  probably accounts for a variety of association bonds, including permanent dipole-induced dipole (47). The values of these components for solvents were calculated from a large number of solubility data sets. Polymer solubility parameters can also be decomposed to a three-term set. The Hansen parameters give improved agreement with data but are still not completely accurate in predicting solution thermodynamics for every system.

The region of solubility is characterized by the distance between solvent and solute coordinates (14)

$$R_{ij} = (4(\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2)^{1/2} \quad (10)$$

If the distance between the solvent and solute Hansen coordinate position exceeds  $R_{ij}$ , the two components are not soluble (or swelling is less than expected).  $R_{ij}$  reduces the need for three-dimensional plots, which were difficult to accomplish in the past. Computer-aided design packages should permit rapid solutions to these problems now. Some investigators have used two-dimensional plots for polar and hydrogen bonding terms, but the technique may be misleading for materials with large dispersion contributions. Barton (12) gives a number of models and contour map examples.

Applications of solubility parameters include finding compatible solvents for coating resins, predicting the swelling of cured elastomers by solvents, estimating solvent pressure in devolatilization and reactor equipment (16), and predicting polymer-polymer (107), polymer-binary (93), random copolymer (102), and multicomponent solvent (38, 98, 108, 109) equilibria.

## 1.3 Relationships between the Solubility Parameter and Other Thermodynamic Parameters

Hildebrand and Hansen parameters can be calculated using other thermodynamic quantities. This section contains some of the thermodynamic relationships for binary systems. Extension to multicomponent systems is described in part by Flory (37) and Olabisi et al. (89).

**Activity Coefficients** The relationships between solvent solubility parameters and solvent activity coefficients using excess free energy calculations on regular solutions are (93)

$$RT \ln \gamma_1 = V_1 \phi_2^2 (\delta_1 - \delta_2)^2 \quad (11)$$

$$RT \ln \gamma_2 = V_2 \phi_1^2 (\delta_1 - \delta_2)^2 \quad (12)$$

Equations 11 and 12 depend on the use of the geometric mean,  $\delta = (\delta_1\delta_2)^{1/2}$ . Funk and Prausnitz (40) show that there are deviations from this rule for aromatic hydrocarbons.

**Partial Excess Free Energy of Mixing** For binary solutions, the partial excess free energy of mixing can be written as

$$\Delta G^E = \sum (\delta_{1i} - \delta_{2i})^2 \quad (13)$$

where  $\delta_{ji}$  = solubility term of group  $i$  for species  $j$ .

**Polymer-Solvent Interaction Parameter** The polymer-solvent interaction parameter has been written as a sum of an entropic and enthalpic component

$$\chi = \chi_S + \chi_H \quad (14)$$

where  $\chi_S$  = entropic term and  $\chi_H$  = enthalpic term of the interaction parameter.  $\chi_S$  is usually taken to be a constant between 0.3 and 0.4 for nonpolar systems ( $\chi_S = 0.34$  is often used) (15, 104). The enthalpic component can be related to the Hildebrand parameters

$$\chi_H = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (15)$$

$$\chi = 0.34 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (16)$$

Equation 15 only allows positive values for  $\chi_H$ .  $\chi < 0.5$  is the Flory-Huggins theory criterion for a polymer and solvent to be completely miscible over the entire composition range. The solubility parameters of the solvent and polymer must be similar for this to occur (21). The molar volume of the solvent also affects miscibility and phase equilibria: a Hildebrand parameter needed for phase separation or miscibility cannot be specified without specifying  $V_1$ . Equation 16 works well for nonpolar systems where Eq. 15 is a good description of the enthalpic portion of the interaction parameter. For polar systems, the geometric mean assumption of regular solution theory is not appropriate, and better models include an extra term describing the interchange energy density for the solvent-solute pair. For example

$$A_{12} = \delta_1^2 + \delta_2^2 - 2l_{12}\delta_1\delta_2 \quad (17)$$

where  $l_{12}$  = characterizes the intermolecular forces between molecules and the geometric mean assumption is not made, and

$$\chi = \chi_S + \frac{V_1 A_{12}}{RT} \quad (18)$$

Equation 17 allows the modelling of specific interactions between components 1 and 2. Mixed solvents can be treated as a single solvent by determining the solubility parameter of the solvent mixture and then using this value in Eq. 16. If both the solvents and the polymers interact, then the description is more complicated.

The two-component solubility parameter can be used to define  $A_{12}$  (25).

$$A_{12} = (\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 \quad (19)$$

The Hansen parameters also could be used to model  $A_{12}$ .

Several recent theories for polymer solution thermodynamics include entropic, enthalpic, and free-volume contributions to the free energy of mixing. For example, Eq. 14 would be modified by including  $\chi_{S(FV)}$  = free-volume (noncombinatorial) contribution to the entropic interaction parameter. The free-volume contribution to entropy has the opposite temperature dependence from the combinatorial term and helps explain the lower critical solution temperature. Assuming that Eq. 15 correctly describes the temperature dependence of the enthalpic contribution, Eq. 16 might not be valid over large temperature ranges because of the assumption,  $\chi_S = 0.34$ .

## 2. CALCULATIONS OF AND CORRELATIONS FOR SOLUBILITY PARAMETERS

Solubility parameters can be determined by direct measurements, correlations with other physical parameters, or indirect calculations. The solubility parameters of solvents usually can be determined directly. The solubility parameters of polymers can only be determined indirectly and may be affected by variations in their chemical constitutions, i.e., the number of crosslinks and the distribution of chain branches or substitutive groups along the polymer backbone. The methods presented in Section 2 can be used to develop correlations of solubility parameters with other physical properties for specific commercial polymer products or to estimate the solubility parameters of new polymers.

### 2.1 Solvents

**Relating the Enthalpy of Vaporization to the Energy of Vaporization.** When  $\Delta H_i^*$  is available at 25°C, Eq. 5 can be used to calculate  $\Delta E_i^*$ . The molar volume of the solute is needed to complete the calculation of  $\delta$  using Eq. 3. This is the most direct and accurate method of determining the solubility parameter. However,  $\delta$ 's determined in this way may not give the best prediction of solution behavior. The values in Tables 3.1-3.3 reflect how the solvents behave in a variety of systems.

**Correlations.** Both the enthalpy of vaporization and the molar volume of a solvent can be estimated from correlations. When  $\Delta H_i^*$  is known at the normal boiling point, it can be converted to the appropriate value at a second temperature using (126)

$$\frac{\Delta H_i^*, T_2}{\Delta H_i^*, T_1} = \left( \frac{T_c - T_2}{T_c - T_1} \right)^{0.38} \quad (20)$$

This corresponding-state-type procedure gives estimates within 2% of experimental values over a wide range of temperatures (35). Hildebrand and Scott (59) proposed an empirical correlation between  $\Delta H_i^*$  at 25°C and the normal boiling point,  $T_b$

$$\Delta H_i^*, 298^\circ\text{K} = 0.2950 + 23.7 T_b + 0.020 T_b^2 \quad (21)$$

where the enthalpy units are kcal/mol. Lawson (67) suggests different coefficients to include fluorocarbon liquids. The Clausius-Clapeyron equation can be applied if vapor pressure data are available. Equation 21 is reasonably accurate only for liquids which are not hydrogen bonded. The Hildebrand parameter calculated by Eq. 21 should be adjusted (24) as follows for

different solvents: add  $1.4 (\text{cal}/\text{cm}^3)^{1/2}$  for alcohols, add  $0.6 (\text{cal}/\text{cm}^3)^{1/2}$  for esters, and add  $0.5 (\text{cal}/\text{cm}^3)^{1/2}$  for ketones if the boiling point is less than  $100^\circ\text{C}$ . Jayasri and Yaseen (64) suggest adding  $1.7 (\text{cal}/\text{cm}^3)^{1/2}$  for alcohols.

Solvent molar volumes are often available or can be calculated by group molar volume methods at  $25^\circ\text{C}$  (35). The molar volume for solids at  $25^\circ\text{C}$  can be extrapolated from liquid state values (the liquid is assumed to be subcooled).

**Thermodynamic Coefficients.** The internal pressure  $\pi$  is defined as (88)

$$\pi = \left( \frac{\delta E}{\delta V} \right) = T\beta - p \quad (22)$$

Since the external pressure is usually small with respect to  $T\beta$ , the internal pressure is approximated by

$$\pi = T\beta = T \frac{\alpha}{\kappa} = T \left( \frac{\delta p}{\delta T} \right) \quad (23)$$

where the constant volume thermal pressure coefficient  $\beta$  is the ratio of the coefficient of thermal expansion  $\alpha$  to the isothermal compressibility  $\kappa$ . The Hildebrand parameter is the square root of the internal pressure; Eq. 23 provides a method for scaling the Hildebrand parameter with temperature. For polymers, this equation provides a method for the direct estimation of  $\delta$  [ $\alpha$  and  $\kappa$  are measurable, where  $\Delta H_i^\circ$  is not meaningful (Eq. 5)]. The thermal pressure coefficient (Eq. 23) can be evaluated from vapor-pressure data and is easier to apply than the Clausius-Clapeyron equation. For applications at high pressure, such as phase equilibria in reverse osmosis membranes, the external pressure term of Eq. 22 may not be negligible. Solubility parameters generally decrease with increasing pressure.

**van der Waals Gas Constant.** Tables are available in many handbooks for the van der Waals correction constants to the ideal gas law,  $a$  and  $b$ , where  $a$  has units of  $(\text{liters})^2 - (\text{atmospheres})$ . For some liquids, these values may be at hand when other data are not available. They can be used to check Hildebrand parameter values obtained from other sources.

$$\delta = 1.2 \frac{a^{1/2}}{V} \quad (24)$$

The form of Eq. 24 can be obtained by substituting the van der Waals equation of state into Eq. 22.

**Critical Pressure.** The solubility parameter is related to the critical pressure  $P_c$  of a substance through the empirical equation

$$\delta = 1.25 P_c^{1/2} \quad (25)$$

where the critical pressure is expressed in atmosphere. Equation 25 is not very accurate, but is simple to apply if critical pressure data are available.

**Surface Tension.** Michaels (83) has shown that the surface tension can be related to the cohesive energy density

$$\frac{\Delta E_i^\circ}{V_i} = A \left( \frac{1}{V_i} \right)^{1/3} \gamma_L \quad (26)$$

where  $\gamma_L$  is the surface tension and  $A$  is a constant. Koenhen and Smolders (65) correlated surface tension and two Hansen parameters

$$\delta_d^2 + \delta_p^2 = 13.8 \left( \frac{1}{V_i} \right)^{1/3} \gamma_L \quad (27)$$

$\delta_h$  is probably not related to the liquid-vapor interfacial energy these interactions do not involve breaking hydrogen bonds. Equation 27 does not describe cyclic compounds, acetonitrile, carboxylic acids, polyfunctional alcohols, and other polar compounds well. Hildebrand and Scott (59) have proposed a different equation, which has been discussed by Lee (68).

**Index of Refraction.** The dispersive Hansen parameter can be related to the index of refraction,  $n_D$  (65, 105):

$$\delta_d = 9.55 n_D - 5.55 \quad (28)$$

The interaction energy between nonpolar molecules should depend on polarizability (London dispersion forces) and therefore the index of refraction.

**Dipole Moment.** Hansen and Skaarup (54) related the polar Hansen parameter to the dielectric constant  $\epsilon$  and the dipole moment  $\mu$

$$\delta_p^2 = \frac{12108}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2) \mu^2 \quad (29)$$

Beerbower and Dicky (14) proposed an empirical relationship.

$$\delta_p^2 = 9.5 \frac{\mu}{V^{1/2}} \quad (30)$$

**Kauri Butanol Values.** Proprietary hydrocarbon solvents are usually mixtures with boiling ranges and unknown molecular weights. Solubility parameters values may be estimated from Kauri butanol values (ASTM Method D1133-54T) using the equation

$$\delta = 6.3 + 0.03(\text{KB}) \quad (31)$$

## 2.2 Polymers

Hildebrand parameters cannot be calculated for polymers from heat of vaporization data because of their nonvolatility. Indirect methods are described below. The solubility parameter values in Tables 3.4-3.6 may only be representative of the given polymer, since variations in compositions can lead to changes in  $\delta$ .

**Solvency Testing (Screening Procedure).** The solvency properties of a commercial polymer can be defined by determining its solubility parameter range for each hydrogen bonding class of

solvents (poor, moderate, and strong). The midpoints of these ranges may be used as single-valued quantities for some purposes, but may not agree with values determined by other methods (43). A gram or two of solid polymer is placed in a test tube and an approximate amount of a selected solvent is added such that the final solution would have about the correct solids content for the expected commercial use, e.g., 50% for alkyds, 20% for vinyls, etc. The exact amount is often unimportant, except for poor solvents. A typical phase diagram for binary polymer-solvent systems may show upper and lower critical solution temperatures. The one-phase region expands away from the UCST and LCST points, which often occur in the range of 20 to 80 wt% polymer. The usual purpose of these experiments is to find good solvents for commercial product formulation, and this screening procedure will help identify such solvents. The mixture may be warmed and stirred to speed up solution, but it should be cooled and observed at room temperature. The resulting mixture should be a single phase, clear and free of gel particles or cloudiness, otherwise the polymer is judged insoluble. The solvents to be used are selected from Table 2.1.

TABLE 2.1 SELECTED SOLVENTS FOR USE IN POLYMER SOLVENCY TESTING ( $\delta$  IN (MPA)<sup>1/2</sup>)

Solvent	$\delta$
POORLY HYDROGEN BONDED	
n-Pentane	14.3
n-Heptane	15.1
Methylcyclohexane	16.0
Solvesso 150	17.4
Toluene	18.2
Tetrahydronaphthalene	19.4
o-Dichlorobenzene	20.5
1-Bromonaphthalene	21.7
Nitroethane	22.7
Acetonitrile	24.1
Nitromethane	26.0
MODERATELY HYDROGEN BONDED	
Diethyl ether	15.1
Diisobutyl ketone	16.0
n-Butyl acetate	17.4
Methyl propionate	18.2
Dibutyl phthalate	19.0
Dioxane	20.3
Dimethyl phthalate	21.9
2,3-Butylene carbonate	24.8
Propylene carbonate	27.2
Ethylene carbonate	30.1
STRONGLY HYDROGEN BONDED	
2-Ethyl hexanol	19.4
Methyl isobutyl carbinol	20.5
2-Ethylbutanol	21.5
n-Pentanol	22.3
n-Butanol	23.3
n-Propanol	24.3
Ethanol	26.0
Methanol	29.7

This grouping of solvents has been selected so that the Hildebrand parameter values increase by reasonably constant steps within each hydrogen bonding class. The object of using these solvent spectra is to establish a solubility parameter range for a polymer rather than a single-valued number. This range has the advantage of showing the difference  $(\delta_1 - \delta_2)^2$  (see Eqs. 11 and 15), which can be tolerated between the solubility values of the polymer and solvent for miscibility. Van Dyk et al. (120) have shown that including the molar volume improves the correlation between solvency and the solubility parameters. A better measure of solubility might be the group,  $V_i(\delta_1 - \delta_2)^2$ , but such values are not now available for a wide range of polymers.

In carrying out the procedure, it is convenient to select the first trials about 1/3 and 2/3 of the way down the column: for example, in the poorly hydrogen bonded group, toluene and nitroethane would be chosen. If the polymer is soluble in both, there is no need to try intermediate solvents because experience has shown that the polymer will be soluble in every case. The solvents at the end of the spectrum should be tried next. If the polymer is soluble in one but not both of the initial trials, the third trial should be half-way between the two. By successive choices, sets of two adjacent solvents will be found, one of which dissolves the polymer and one which does not. The parameter values of the solvents which do dissolve the polymer mark the ends of the range. The procedure is repeated for the other two hydrogen bonding classes.

**Swelling Values.** Another method for measuring the solubility parameter of polymers is to prepare a sparsely crosslinked form and immerse samples in a series of liquids of varying  $\delta$ . The crosslinked material will swell to varying degrees. The amount of swelling can be measured by length, weight, or volume changes. The amount of swelling should be at a maximum when the solvent has the same Hildebrand parameter as the polymer. By inference, the soluble, uncrosslinked material has the same value. An example of a crosslinked sample is styrene polymerized with 1% divinyl benzene.

**Refractive Index.** Koenhen and Smolders (65) have predicted dispersive Hansen parameters from refractive index measurement on polymers. Wu (127) has suggested an effective cross-sectional area to relate the cohesive energy density and surface tension.

$$\delta_d^2 = A \left( \frac{n_s}{V_{i,s}} \right)^{1/3} \gamma_s^d \quad (32)$$

where  $n_s$  = number of atoms in a segment,  $V_{i,s}$  = molar volume of a segment, and  $\gamma_s^d$  = dispersion contribution to the free surface energy of the polymer.

**Dipole Moment.** Equation 29 has successfully applied to polymers by Koenhen and Smolders (65). The dipole moments of polymers are between 70 and 90% of those of the corresponding monomer units.

**Hydrogen-Bonding Parameter.** Hansen and Beerbower (55) compiled enthalpy data for hydrogen bonding groups. The following values are suggested:

Group	Cohesive energy $E_h$ , kJ mol <sup>-1</sup>	Refs.
Alcohol	20.9	—
Amide	16.3	83
Ester	5.2	54
Nitrile	2.1	54
Ether	2.3	54
Monochloro substituent	0.4	54
Phenylene ring	0.4	54

The hydrogen-bonding parameter is given by

$$\delta_h^2 = \frac{E_h}{V_i} \quad (33)$$

**Intrinsic Viscosity.** A number of researchers have used intrinsic viscosity to estimate Hildebrand parameters. Flory (37) related intrinsic viscosity to polymer molecular weight and the chain-expansion factor. The chain-expansion factor can, in turn, be related to the polymer-solvent interaction parameter using the Flory-Huggins theory. A variety of models can be used to relate the interaction parameter to Hildebrand parameters (19, 80, 115). These equations have the form

$$[\eta] = K_1 - K_2 V_i^n \Delta \delta^2 \quad (34)$$

where  $[\eta]$  intrinsic viscosity,  $K_i$  = constants, and  $n$  is either 1/2 or 1 (120). These researchers have shown that Eq. 34 gives a good correlation between solvency and Hansen parameters for methacrylate polymers.

**Inverse Phase Gas Chromatography.** Inverse phase gas chromatography has been used by a number of investigators to measure infinite dilution weight fraction activity coefficients (6, 29–31, 63, 71–72, 84, 90–91, 113). These coefficients can be related to Hildebrand parameters by using a thermodynamic theory for polymer solutions, such as Flory-Huggins theory. The polymer is the stationary phase in a gas chromatography column. Both binary and multicomponent equilibria (46, 99, 100) can be studied using this method. Chromatographic techniques have the advantage of rapid measurement of thermodynamic values once the columns have been made. Both  $V_i$  and  $\Delta H_i^V$  must be known at the temperature of the column. Molar volumes for the solvents can be determined by using literature density equations or generating equations from density data. Values for the enthalpy of vaporization can be determined at the experimental temperature (71).

The inverse phase gas chromatography method has the advantage of providing values for  $\delta_2^*$  over a range of temperatures. This is particularly valuable for the prediction of phase equilibria at elevated temperatures. The value of  $\delta_2^*$  at 25°C can be estimated by using the expected temperature dependence for  $\chi$  (Eq. 16) of

$$\chi = \alpha + \beta/T \quad (35)$$

One potential problem with this technique is that  $\chi$  is known to be a function of concentration and the polymer Hildebrand parameter is determined at infinite dilution of solvent. For a number of binary systems, the change in  $\chi$  with solvent weight fraction is the largest as  $\omega_1 \rightarrow 0$ . The concentration dependence of  $\chi$  may increase as  $\chi$  increases, so that systems with moderate or strong enthalpic interactions may not be modelled well.

### 2.3 Group Contribution Methods

Group contribution methods have been applied to the problem of estimating the solubility parameter (17, 20, 28, 33, 35, 58, 60–61, 96, 112, 121–122). van Krevelen (123), Fedors (35), and Barton (12) have reviewed these techniques and give tables of group values. The molar volume of solvents and polymers can also be estimated by a group contribution technique (108).

The sets of group constants of Small (112), Hoy (61), van Krevelen (121), and van Krevelen and Hoftyzer (122) seem to be most comprehensive. Table 2.2 gives the group molar attraction constants at 25°C. Small's values were derived from measurements of the heat of vaporization. Hoy's values were derived from vapor pressure measurements. The group contribution values of van Krevelen and Hoftyzer are based on cohesive energy data of polymers.

The group contribution techniques are based on the assumption that the contributions of different functional groups to the thermodynamic property are additive. The energy of vaporization of a solvent or polymer is

$$\Delta E_i^V = \sum_j n_j \Delta e_j \quad (36)$$

where  $\Delta e_j$  is the energy of vaporization contribution of group  $j$  and  $n_j$  is the number of groups of type  $j$  in the molecule. The solubility parameter is obtained by combining Eqs. 42 and 43

$$\delta_i = \left( \frac{\Delta E_i^V}{V_i} \right)^{1/2} = \left( \frac{\sum_j n_j \Delta e_j}{V_i} \right)^{1/2} \quad (37)$$

Small (112) defined the molar attraction constant as

$$F_j = (\Delta E_{i,j}^V V_{i,j})^{1/2} \quad (38)$$

which can be used to calculate the solubility parameter by

$$\delta_i = \left( \frac{\Delta E_i^V V_i}{V_i^2} \right)^{1/2} = \frac{\sum_j F_j}{V_i} = \frac{\sum_j \rho_j F_j}{M_i} \quad (39)$$

where  $\rho_i$  is polymer density and  $M_i$  is polymer molecular weight. For polymers,  $\delta_i$  can be evaluated for the repeating group by using group contribution calculations for the molar volume and the cohesive energy density or molar attraction constant.



TABLE 2.2 GROUP CONTRIBUTIONS TO COHESIVE ENERGY DENSITY<sup>a</sup>

Group	F [(MPa) <sup>1/2</sup> cm <sup>3</sup> mol <sup>-1</sup> ]			ΔE <sub>i</sub> <sup>*</sup> (J mol <sup>-1</sup> ) van Krevelen and Hoftyzer (122)
	Small (112)	van Krevelen (121)	Hoy (61)	
CARBON-CONTAINING GROUPS				
CH <sub>3</sub>	437	420	303	9630
·CH <sub>2</sub>	272	280	269	4190
·CH-	57	140	176	419
·C=	-190	0	65	-6700
·CH <sub>2</sub>	388	—	259	—
·CH-	227	222	249	—
·C<	39	82	173	—
CH=(aromatic)	—	—	240	—
·C=(aromatic)	—	—	201	—
CH(CH <sub>3</sub> )-	495	560	(479)	—
C(CH <sub>3</sub> ) <sub>2</sub> -	685	841	(672)	(10000)
CH=CH-	454	444	497	(12600)
C=CH-	265	304	421	8374
(CH <sub>3</sub> )=CH-	(704)	724	(725)	1675
IC≡C-	583	—	—	(11300)
·C≡C-	454	—	—	—
cyclopentyl	—	1380	1300	—
cyclohexyl	—	1660	1470	—
phenyl	1500	1520	(1400)	—
phenylene	1350	1380	(1440)	28500
naphthyl	2340	—	—	25100
OXYGEN-CONTAINING GROUPS				
·O-(ether)	143	255	235	6280
(epoxide)	—	—	360	—
OH	—	754	462	—
(aromatic)	—	—	350	—
CO-	562	685	538	—
·CHO	—	—	599	—
·OO-	634	511	688	—
·OOH	—	651	(998)	13400
·O-(C=O)-O-	—	767	(904)	—
C=O)-O-(C=O)-	—	767	1160	—
NITROGEN-CONTAINING GROUPS				
·NH <sub>2</sub>	—	—	464	—
·NH-	—	—	368	—
·N<	—	—	125	—
·HCN	(896)	1120	(901)	(28900)
·N	839	982	725	28500
C=O)-NH-	—	1290	(906)	60700
·O-(C=O)-NH-	—	1480	(1040)	—
·N=C=O	—	—	734	—
OTHER GROUPS				
I	164-205	140	-103(acidic dimer)	—
·I-	460	460	428	6280
·H	644	—	—	—
·I(primary)	(250)	164	84	5020
·I(primary)	552	471	420	13000
·I(primary)	695	614	528	15500
·F <sub>2</sub> -	870	—	—	—
·F <sub>3</sub>	307	—	—	—
·N=O	561	—	—	—
·O <sub>2</sub>	900	—	—	—
·O <sub>4</sub>	900	—	—	—
i-	1020	—	—	—
	-77	—	—	—

Group	F [(MPa) <sup>1/2</sup> cm <sup>3</sup> mol <sup>-1</sup> ]			$\Delta E_i^*$ (J mol <sup>-1</sup> ) van Krevelen and Hoftyzer (122)
	Small (112)	van Krevelen (121)	Hoy (61)	
STRUCTURAL FEATURES				
Conjugation	41-61	—	48	—
cis	—	—	-15	—
trans	—	—	-28	—
Ring —4	—	—	159	—
5	215-235	—	43	—
6	194-215	—	-48	—
Subscription				
ortho	—	—	20	—
meta	—	—	14	—

A -Values in parentheses are calculated from other literature values (122).

Small's constants should not be used for alcohols, amines, carboxylic acids, or other strongly hydrogen bonded compounds unless such functional groups constitute only a small part of the molecule so that the proportional error is not great. Small's constants should be compatible with data in Tables 3.1 and 3.2, which were calculated from latent heats or approximated from actual boiling points. Hoy's constants are based on vapor pressure measurements and should be used with solvent solubility parameters derived from vapor pressure data. The differences between experimental and calculated solubility values is usually less than 10% (35), but special care should be taken with complex ring compounds. Ahmad and co-workers have calculated solubility parameters for a number of polymers (1-5).

### 3. SOLUBILITY PARAMETER TABLES

Tables 3.1 and 3.2 contain data on a wide variety of liquids. The values are based on heats of vaporization, with corrections applied as described in Section 2.1. Values for commercial mixed hydrocarbon solvents were estimated from published Kauri butanol values. Hansen parameters for solvents and polymers are given in Tables 3.3 and 3.6. Values for commercial polymers are given in Tables 3.4 and 3.5 and are consistent with the solvent data in Tables 3.1 and 3.2. The single values given in Table 3.5 have been obtained by different methods; the original reference should be checked prior to using any particular value.

TABLE 3.1 SOLUBILITY PARAMETERS OF SOLVENTS: ALPHABETICAL LIST

Solvent	$\delta$ [(MPa) <sup>1/2</sup> ]	$\delta$ [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ]	H-Bonding Group
Acetaldehyde	21.1	10.3	m
Acetic acid	20.7	10.1	s
Acetic anhydride	21.1	10.3	s
Acetone	20.3	9.9	m
Acetonitrile	24.3	11.9	p
Acetophenone	21.7	10.6	m
Acetyl chloride	19.4	9.5	m
Acetylmorpholine (N)	23.7	11.6	m
Acetypiperidine (N)	22.9	11.2	s
Acetypyrrolidine(N)	23.3	11.4	s
Acrolein	20.1	9.8	s
Acrylic acid	24.6	12.0	s
Acrylonitrile	21.5	10.5	p
Allyl acetate	18.8	9.2	m
Allyl alcohol	24.1	11.8	s
Allyl chloride	18.0	8.8	m
Ammonia	33.4	16.3	s
Amyl acetate (iso)	16.0	7.8	m
(normal)	17.4	8.5	m
(secondary)	17.0	8.3	m
Amyl alcohol	20.5	10.0	s
(normal)	22.3	10.9	s

Solvent	Molar volume	Solubility Parameters			
	[cm <sup>3</sup> /mol] V	$\delta_D$	$\delta_P$	$\delta_H$	$\delta$
POLYHYDRIC ALCOHOLS					
Ethylene glycol	55.8	17.0	11.0	26.0	32.9
Glycerol	73.8	17.4	12.1	29.3	36.2
Propylene glycol	73.6	16.8	9.4	23.3	30.3
1,3-Butanediol	89.9	16.6	10.0	21.5	28.8
Diethylene glycol	95.3	16.2	14.7	20.5	29.9
Triethylene glycol	114.0	16.0	12.5	18.6	27.4
Hexylene glycol	123.0	15.8	8.4	17.8	25.2
Dipropylene glycol <sup>d</sup> (mixed isomers)	131.3	16.0	20.3	18.4	31.7

<sup>a</sup> Altered from previously published value.<sup>b</sup> Solid, treated as supercooled liquid.<sup>c</sup> Values uncertain.<sup>d</sup> Impure commercial product of this nominal formula.

TABLE 3.4 SOLUBILITY PARAMETER RANGES OF COMMERCIAL POLYMERS\* (CHEMICAL COMPOSITION ADDED WHEREVER KNOWN)

Polymer	$\delta$ in [(MPa) <sup>1/2</sup> ] Solvent Hydrogen Bonding			$\delta$ in [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ] Solvent Hydrogen Bonding		
	Poor	Moderate	Strong	Poor	Moderate	Strong
POLY(ACRYLICS)						
Acryloid B-44	18.2-24.3	17.4-27.2	0	8.9-11.9	8.5-13.3	0
Acryloid B-66 (MMA/BMA copolymer)	17.4-22.7	16.0-24.8	0	8.5-11.1	7.8-12.1	0
Acryloid B-72 (EMA/MA copolymer)	17.4-26.0	18.2-26.0	0	8.5-12.7	8.9-13.3	0
Acryloid B-82 (EA/MMA copolymer)	17.4-22.7	18.2-24.8	0	8.5-11.1	8.9-12.1	0
Poly(butyl acrylate)	14.3-26.0	15.1-24.8	19.4-26.0	7.0-12.7	7.4-12.1	9.5-12.7
Poly(isobutyl methacrylate)	17.4-22.7	17.4-20.3	19.4-23.3	8.5-11.1	8.5-9.9	9.5-11.4
Poly(n-butyl methacrylate)	15.1-22.7	15.1-20.3	19.4-23.3	7.4-11.1	7.4-9.9	9.5-11.4
Poly(ethyl methacrylate)	17.4-22.7	16.0-27.2	19.4-23.3	8.5-11.1	7.8-13.3	9.5-11.4
Poly(methacrylic acid)	0	20.3	26.0-29.7	0	9.9	12.7-14.5
Poly(methyl methacrylate)	18.2-26.0	17.4-27.2	0	8.9-12.7	8.5-13.3	0
80 BMA/20 An	17.4-26.0	16.0-25.0	0	8.5-12.7	7.8-12.2	0
75 Isobornyl MA/25 C	15.1-21.7	15.1-17.4	19.4-22.3	7.4-10.6	7.4-8.5	9.5-10.9
20 MAA/80 —Blown linseed oil	17.4	0	0	8.5	0	0
15 MAA/38 EA/47 S	19.4	17.4-18.2	0	9.5	8.5-8.9	0
15 MAA/27.5 MA/57.5 VAc	0	20.3-30.1	26.0-29.7	0	9.9-14.7	12.7-14.5
15 MAA/17.5 MA/67.8 VAc	0	20.3-30.1	26.0-29.7	0	9.9-14.7	12.7-14.5
58 MAA/42 C	19.4	17.4-25.0	0	9.5	8.5-12.2	0
50 MMA/50 EA	17.4-26.0	16.0-27.0	0	8.5-12.7	7.8-13.2	0
25 MMA/75 EA	0	18.2-22.1	19.4-29.7	0	8.9-10.8	9.5-14.5
40-MMA/40-EA/20-AGE	17.4-26.0	16.0-27.0	21.5	8.5-12.7	7.8-13.2	10.5
45 MMA/45 EA/10 AM	22.7-26.0	18.2-27.0	26.0-29.7	11.1-12.7	8.9-13.2	12.7-14.5
55 MMA/30 EA/15 An	21.7-26.0	17.4-20.3	0	10.6-12.7	8.5-9.9	0
40 MMA/40 EA/20 An	21.7-26.0	19.0-30.1	0	10.6-12.7	9.3-14.7	0
40 MMA/40 EA/20 tBAMA	17.4-26.0	16.0-27.0	19.4-29.7	8.5-12.7	7.8-13.2	9.5-14.5
40 MMA/40 EA/20 C	17.4-26.0	16.0-27.0	20.5-22.3	8.5-12.7	7.8-13.2	10.0-10.9
40 MMA/40 EA/20 MAA	0	18.2-22.1	19.4-29.7	0	8.9-10.8	9.5-14.5
45 MMA/45 EA/10 mAm	17.4-26.0	17.4-27.0	26.0-29.7	8.5-12.7	8.5-13.2	12.7-14.5
40 MMA/40 EA/20 VBE	17.4-26.0	16.0-27.0	26.0	8.5-12.7	7.8-13.2	12.7
Pacrosir 9055, 50% (SIR)						
in 50% solutions	16.0-22.7	15.1-22.1	19.4-26.0	7.8-11.1	7.4-10.8	9.5-12.7
in 1% solutions	17.4-22.7	15.1-22.3	19.4-24.8	8.5-11.1	7.4-10.9	9.5-12.1

\* Note: See end of Table 3.4 for monomer identification (page VII-550).

Polymer	$\delta$ in [(MPa) <sup>1/2</sup> ] Solvent Hydrogen Bonding			$\delta$ in [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ] Solvent Hydrogen Bonding		
	Poor	Moderate	Strong	Poor	Moderate	Strong
ALKYD RESINS						
40% Adipic, glycerol phthalate	22.7-26.0	20.3-30.1	26.0-29.7	11.1-12.7	9.9-14.7	12.7-14.5
45% Linseed, glycerol phthalate	14.3-24.3	15.1-22.1	19.4-24.3	7.0-11.9	7.4-10.8	9.5-11.9
28% Soy, glycerol phthalate	17.4-22.7	17.4-27.0	0	8.5-11.1	8.5-13.2	0
30% Soy, glycerol phthalate	17.4-26.0	17.4-30.1	0	8.5-12.7	8.5-14.7	0
45% Soy, glycerol phthalate	14.3-22.7	15.1-22.1	19.4-24.3	7.0-11.1	7.4-10.8	9.5-11.9
38% Soy-DHC, glycerol oil modified alkyd	17.4-22.7	16.0-24.8	20.5-23.3	8.5-11.1	7.8-12.1	10.0-11.4
45% Soy, pentaerythritol phthalate	14.3-22.7	15.1-22.1	19.4-24.3	7.0-11.1	7.4-10.8	9.5-11.9
Methacrylated DHC, PE alkyd	17.4-22.1	17.4-27.0	0	8.5-11.1	8.5-13.2	0
Pelargonic alkyd	17.4-22.1	16.0-24.8	0	8.5-11.1	7.8-12.1	0
PE Phthalate benzoate	19.4-26.0	17.4-30.1	0	9.5-12.7	8.5-14.7	0
PE Tri-(p-tert)-butyl benzoate mono acid phthalate	17.4-26.0	15.1-20.3	19.4-23.3	8.5-12.7	7.4-9.9	9.5-11.4
PE p-tert-butyl benzoate phthalate	17.4-22.7	16.0-27.2	20.5-22.3	8.5-11.1	7.8-13.3	10.0-10.9
Restiroid 3030, 60% (SIR)						
in 50% solutions	16.0-22.7	15.1-20.3	0	7.8-11.1	7.4-9.9	0
in 1% solutions	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Restoroid 3751, 50% (SIR)						
in 50% solutions	17.4-22.7	15.1-22.1	21.5-23.3	8.5-11.1	7.4-10.8	10.5-1.4
in 1% solutions	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Siralkid 2240, 100% (SIR)						
in 50% solutions	16.8-21.7	19.0	0	8.2-10.6	9.3	0
in 1% solutions	17.4-21.7	0	0	8.5-10.6	0	0
Siralkid 2256, 100% (SIR)						
in 50% solutions	14.3-22.7	15.1-20.3	19.4-22.3	7.0-11.1	7.4-9.9	9.5-10.9
in 1% solutions	16.0-22.7	16.0-20.3	0	7.8-11.1	7.8-9.9	0
Siralkid 2287/AV, 100% (SIR)						
in 50% solutions	16.0-22.7	18.2-20.3	19.4-22.3	7.8-11.1	8.9-9.9	9.5-10.9
in 1% solutions	16.8-21.7	18.2-20.3	21.5	8.2-10.6	8.9-9.9	10.5
Siralkid 2550, 100% (SIR)						
in 50% solutions	15.1-22.7	15.1-20.3	19.4-22.3	7.4-11.1	7.4-9.9	9.5-10.9
in 1% solutions	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Siralkid 2669, 100% (SIR)						
in 50% solutions	14.3-22.7	15.1-20.3	19.4-24.3	7.0-11.1	7.4-9.9	9.5-11.9
in 1% solutions	14.3-21.7	15.1-20.3	19.4-22.3	7.0-10.6	7.4-9.9	9.5-10.9
AMINE RESINS						
Beckamine P-196 (urea-formaldehyde)	18.2-22.7	17.4-22.1	19.4-26.0	8.9-11.1	8.5-10.8	9.5-12.7
Beetle 227-8 (urea-formaldehyde)	0	0	18.2-23.3	0	0	8.9-11.4
Cyzak 1006 (melamine-formaldehyde)	17.4-22.7	16.0-27.2	21.5-22.3	8.5-11.1	7.8-13.3	10.5-10.9
Cyzak 1007 (melamine-formaldehyde)	17.4-22.7	17.4-27.2	0	8.5-11.1	8.5-13.3	0
Cyzak 1013 (melamine-formaldehyde)	17.4-22.7	16.0-24.8	0	8.5-11.1	7.8-12.1	0
Cyzak 1026 (melamine-formaldehyde)	0	18.2-27.0	0	0	8.9-13.2	0
Hexa (methoxy methyl) melamine	17.4-24.1	17.4-30.1	19.4-33.8	8.5-11.8	8.5-14.7	9.5-16.5
Resimene 888 (melamine-formaldehyde)	17.4-21.7	15.1-24.8	19.4-26.0	8.5-10.6	7.4-12.1	9.5-12.7
Siramin 4147, 67% (SIR)						
in 50% solutions	15.1-23.3	15.1-22.1	18.6-29.7	7.4-11.4	7.4-10.8	9.1-14.5
in 1% solutions	17.4-22.7	15.1-22.1	19.4-26.0	8.5-11.4	7.4-10.8	9.5-12.7
Siramin 6150, 60% (SIR)						
in 50% solutions	14.3-26.0	15.1-27.2	18.6-29.7	7.0-12.7	7.4-13.3	9.1-14.5
in 1% solutions	14.3-21.7	16.0-22.1	19.4-29.7	7.0-10.6	7.8-10.8	9.5-14.5
Versalon 1112 dimer acid-polyamine	0	0	19.4-23.3	0	0	9.5-11.4
Versalon 1175	0	0	19.4-23.3	0	0	9.5-11.4
Versamid 100 dimer acid-polyamine	17.4-21.7	17.4-18.2	19.4-23.3	8.5-10.6	8.5-8.9	9.5-11.4
Versamid 115	17.4-21.7	16.0-20.3	19.4-26.0	8.5-10.6	7.8-9.9	9.5-12.7
Versamid 930	0	0	19.4-23.3	0	0	9.5-11.4
Versamid 940	0	0	19.4-23.3	0	0	9.5-11.4
Uformite MX-61 (benzoguamine-formaldehyde)	17.4-22.7	15.1-22.7	19.4-22.7	8.5-11.1	7.4-11.1	9.5-11.1

Polymer	$\delta$ in [(MPa) <sup>1/2</sup> ] Solvent Hydrogen Bonding			$\delta$ in [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ] Solvent Hydrogen Bonding		
	Poor	Moderate	Strong	Poor	Moderate	Strong
CELLULOSE DERIVATIVES						
Alcohol soluble butyrate	24.1	17.4-27.0	23.3-29.7	11.8	8.5-13.2	11.4-14.5
Cellulose acetate, LL-1	22.7-26.0	20.3-30.1	0	11.1-12.7	9.9-14.7	0
Cellulose Acetate-butyrates	22.7-26.0	17.4-30.1	26.0-29.7	11.1-12.7	8.5-14.7	12.7-14.5
Cellulose butyrate, 0.5 sec	22.7-26.0	17.4-30.1	26.0-29.7	11.1-12.7	8.5-14.7	12.7-14.5
Cyanoethyl cellulose	22.7-26.0	25.0-30.1	0	11.1-12.7	12.2-14.7	0
Ethyl cellulose, K-200	0	17.4-22.1	19.4-23.3	0	8.5-10.8	9.5-11.4
Ethyl cellulose, N-22	16.6-22.7	15.1-22.1	19.4-29.7	8.1-11.1	7.4-10.8	9.5-14.5
Ethyl cellulose, T-10	17.4-19.4	16.0-20.1	19.4-23.3	8.5-9.5	7.8-9.8	9.5-11.4
Ethyl hydroxyethyl cellulose	16.6-21.3	16.4-21.3	0	8.1-10.4	8.0-10.4	0
Nitrocellulose, RS, 25 cps	22.7-26.0	16.0-30.1	29.7	11.1-12.7	7.8-14.7	14.5
Nitrocellulose, SS, 0.5 sec	22.7-26.0	16.0-30.1	26.0-29.7	11.1-12.7	7.8-14.7	12.7-14.5
EPOXY RESINS (EPICHLOROHYDRIN-BISPHENOL A)						
Den 428	18.2	18.2-26.0	0	8.9	8.9-12.7	0
Epon E-72	17.4-21.7	15.1-20.3	19.4-23.3	8.5-10.6	7.4-9.9	9.5-11.4
Epon 812	18.2-26.0	16.0-30.1	20.5-29.7	8.9-12.7	7.8-14.7	10.0-14.5
Epon 864	19.4-26.0	17.4-30.1	0	9.5-12.7	8.5-14.7	0
Epon 1001	21.7-22.7	17.4-27.2	0	10.6-11.1	8.5-13.3	0
Epon 1004	0	17.4-27.2	0	0	8.5-13.3	0
Epon 1007	0	17.4-27.2	0	0	8.5-13.3	0
Epon 1009	0	17.4-20.3	0	0	8.5-9.9	0
Epon 1004 modified soy ester	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Epon 1004 DHC ester	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Eposir 7120, 100% (SIR)						
in 50% solutions	17.4-26.0	15.1-30.1	0	8.5-12.7	7.4-14.7	0
in 1% solutions	19.4-22.7	17.4-27.2	0	9.5-11.1	8.5-13.3	0
Eposir 7161, 100% (SIR)						
in 50% solutions	18.2-22.7	17.4-30.1	0	8.9-11.1	8.5-14.7	0
in 1% solutions	21.7	18.2-27.2	0	10.6	8.9-13.0	0
Eposir 7170, 100% (SIR)						
in 50% solutions	20.5-22.7	17.4-30.1	0	10.0-11.1	8.5-14.7	0
in 1% solutions	0	17.4-27.2	0	0	8.5-13.3	0
Esposir 7180, 100% (SIR)						
in 50% solutions	21.7	17.4-27.2	0	10.6	8.5-13.3	0
in 1% solutions	0	18.2-22.1	0	0	8.9-10.8	0
Esposir 7190, 100% (SIR)						
in 50% solutions	0	17.4-27.2	0	0	8.5-13.3	0
in 1% solutions	0	18.2-22.1	0	0	8.9-10.8	0
Epoester 7842, 100% (SIR)						
in 50% solutions	17.4-22.7	15.1-22.1	21.5	8.5-11.1	7.4-10.8	10.5
in 1% solutions	17.4-21.7	16.0-20.3	0	8.5-10.6	7.8-9.9	0
HYDROCARBON RESINS						
Alpex (cyclized rubber)	15.1-21.7	16.0	0	7.4-10.6	7.8	0
Gilsonite Brilliant Black	16.0-21.7	16.0-17.4	0	7.8-10.6	7.8-8.5	0
Gilsonite Selects	16.0-19.4	16.0-17.4	19.4	7.8-9.5	7.8-8.5	9.5
Hydroxyethylated Nebony 100	17.4-21.7	19.0-20.3	0	8.5-10.6	9.3-9.9	0
Hydroxylated Nebony 100	17.4-21.7	19.0	0	8.5-10.6	9.3	0
Nebony 100	17.4-21.7	16.0-20.3	0	8.5-10.6	7.8-9.9	0
90% Nebony 100/10% paraformaldehyde	17.4-21.7	15.1-20.3	0	8.5-10.6	7.4-9.9	0
50% Nebony 100/50% rosin	16.0-22.7	15.1-20.3	19.4-23.3	7.8-11.1	7.4-9.9	9.5-11.4
Nevchem 100	14.9-21.9	15.1-20.3	0	7.3-10.7	7.4-9.9	0
Nevchem 140	14.9-22.7	15.1-21.9	0	7.3-11.1	7.4-10.7	0
Nevex 100	13.7-22.7	15.1-21.9	0	6.7-11.1	7.4-10.7	0
Nevillac 10°	13.7-26.0	15.1-31.7	18.6-29.7	6.7-12.7	7.4-15.5	9.1-14.5
Nevillac hard	15.6-26.0	15.1-31.7	18.6-29.7	7.6-12.7	7.4-15.5	9.1-14.5
Nevillac soft	15.6-26.0	15.1-31.7	18.6-29.7	7.6-12.7	7.4-15.5	9.1-14.5

Polymer	$\delta$ in [(MPa) <sup>1/2</sup> ] Solvent Hydrogen Bonding			$\delta$ in [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ] Solvent Hydrogen Bonding		
	Poor	Moderate	Strong	Poor	Moderate	Strong
Neville LS685 (cumaarone type)	15.1-21.7	19.0-20.3	0	7.4-10.6	9.3-9.9	0
Nevindene R-1	16.0-22.7	15.1-21.9	0	7.8-11.1	7.4-10.7	0
Nevindene R-7	15.6-21.7	15.1-21.9	0	7.6-10.6	7.4-10.7	0
Nevinol A	13.7-26.0	15.1-24.3	19.4-22.9	6.7-12.7	7.4-11.9	9.5-11.2
Nevpene	13.7-21.7	15.1-17.8	0	6.7-10.6	7.4-8.7	0
Panarez 3-210	17.4-21.7	0	0	8.5-10.6	0	0
Petrolatum 125 HMP	17.4-18.2	0	0	8.5-8.9	0	0
Pliolite NR (cyclized rubber)	17.4-21.7	0	0	8.5-10.6	0	0
Pliolite P-1230	19.4-21.7	0	0	9.5-10.6	0	0
PHENOLIC RESINS						
Amberol F-7 (rosin modified)	17.4-21.7	16.0-20.1	19.4-22.1	8.5-10.6	7.8-9.8	9.5-10.8
Amberol M-82 (rosin modified)	15.1-20.7	15.1-20.3	19.4-22.3	7.4-10.1	7.4-9.9	9.5-10.9
Bakelite BKR-2620	0	17.2-30.1	19.4-29.7	0	8.4-14.7	9.5-14.5
Bakelite CKR-2400	18.2-24.3	16.0-27.2	19.4-29.7	8.9-11.9	7.8-13.3	9.5-14.5
Bakelite CKR-5254	17.4-20.5	16.0-27.2	19.4-22.1	8.5-10.0	7.8-13.3	9.5-10.8
Bakelite CKR-5360	17.4-22.7	16.0-27.2	19.4-23.3	8.5-11.1	7.8-13.3	9.5-11.4
Durez 220 (terpene modified)	17.4-21.7	16.0-20.1	19.4-23.3	8.5-10.6	7.8-9.8	9.5-11.4
Durez 550	14.3-24.3	15.1-20.1	19.4-29.7	7.0-11.9	7.4-9.8	9.5-14.5
Methylon 75202 (allyl phenol)	0	18.2-24.8	0	0	8.9-12.1	0
Sirfen S 1248, 49% (SIR)						
in 50% solutions	24.1-26.0	20.3-30.1	22.3-29.7	11.8-12.7	9.9-14.7	10.9-14.5
in 1% solutions	0	15.1-30.1	22.3-29.7	0	9.9-14.7	10.9-14.5
Sirfen S 1828, 60% (SIR)						
in 50% solutions	18.2-26.0	15.1-30.1	22.3-29.7	8.9-12.7	7.4-14.7	10.9-14.5
in 1% solutions	24.1	17.4-30.1	19.4-29.7	11.8	8.5-14.7	9.5-14.5
Sirfen S 4551, 59% (SIR)						
in 50% solutions	18.2-26.0	15.1-30.1	19.4-29.7	8.9-12.7	7.4-14.7	9.5-14.5
in 1% solutions	0	16.0-30.1	19.4-26.0	0	7.8-14.7	9.5-12.7
Sirfen F 2620, 41% (SIR)						
in 50% solutions	0	22.1	29.7-47.9	0	10.8	14.5-23.4
in 1% solutions	0	22.1	29.7-47.9	0	10.8	14.5-23.4
Sirfen O 1100, 100% (SIR)						
in 50% solutions	22.7-26.0	15.1-30.1	19.4-29.7	11.1-12.7	7.4-14.7	9.5-14.5
in 1% solutions	0	16.0-30.1	19.4-29.7	0	7.8-14.7	9.5-14.5
Sirfenol 5112, 100% (SIR)						
in 50% solutions	15.1-21.7	15.1-20.3	19.4-23.3	7.4-10.6	7.4-9.9	9.5-11.4
in 1% solutions	16.0-21.7	15.1-20.3	19.4-21.5	7.8-10.6	7.4-9.9	9.5-10.5
Sirfenol 5470, 100% (SIR)						
in 50% solutions	17.4-21.7	18.2-20.3	20.9-23.3	8.5-10.6	8.9-9.9	10.2-11.4
in 1% solutions	17.4-20.5	18.2-20.3	20.9-22.3	8.5-10.0	8.9-9.9	10.2-10.9
POLY(ESTERS)						
Acid DEG maleate-phthalate	22.7-26.0	15.1-30.1	19.4-29.7	11.1-12.7	7.4-14.7	9.5-14.5
Carboxyl Terminated DEG phthalate-isophthalate	22.7-26.0	17.8-30.1	0	11.1-12.7	8.7-14.7	0
Cryplex resin 1473-5	18.2-22.7	17.4-27.0	0	8.9-11.1	8.5-13.2	0
Diethylene glycol isophthalate	21.7-26.0	25.0-30.1	0	10.6-12.7	12.2-14.7	0
Diethylene glycol phthalate	22.7-26.0	20.3-30.1	0	11.1-12.7	9.9-14.7	0
Dipropylene glycol phthalate	19.4-26.4	17.4-30.1	0	9.5-12.9	8.5-14.7	0
Dow X-2635 adipate-terephthalate	19.4-26.0	17.4-27.0	0	9.5-12.7	8.5-13.2	0
Dow X-2635 maleate	0	8.22-20.3	0	0	4.0-9.9	0
Hydrogenated bisphenol A fumarate-isophthalate	0	16.0-20.3	0	0	7.8-9.9	0
Hydrogenated bisphenol A-PG fumarate-isophthalate	18.2-22.7	17.4-20.3	0	8.9-11.1	8.5-9.9	0
PE benzoate-maleate	22.7	17.4-30.1	0	11.1	8.5-14.7	0
Siral 5849 100% (SIR)						
in 50% solutions	16.8-21.7	15.1-20.3	19.4-21.5	8.2-10.6	7.4-9.9	9.5-10.5
in 1% solutions	17.4-21.7	16.0-20.3	19.4	8.5-10.6	7.8-9.9	9.5
Soluble mylars (PET) 49000	21.7-22.7	21.7-22.7	0	10.6-11.1	10.6-11.1	0
49001	18.2-21.7	19.0-20.3	0	8.9-10.6	9.3-9.9	0
49002	19.4-21.7	19.0-20.3	0	9.5-10.6	9.3-9.9	0

Polymer	$\delta$ in [(MPa) <sup>1/2</sup> ]			$\delta$ in [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ]		
	Solvent Hydrogen Bonding			Solvent Hydrogen Bonding		
	Poor	Moderate	Strong	Poor	Moderate	Strong
TEG-EG maleate-terephthalate	21.7-24.1	17.4-29.1	0	10.6-11.8	8.5-14.2	0
Triethylene glycol maleate	22.7-26.0	20.3-27.0	0	11.1-12.7	9.9-13.2	0
Varez 123	22.7-24.1	17.4-27.0	19.4-26.0	11.1-11.8	8.5-13.2	9.5-12.7
Vitel PE 100-X linear polyester	22.7	20.3	0	11.1	9.9	0
Vitel PE 101-X	19.4-21.7	20.3-22.1	0	9.5-10.6	9.9-10.8	0
POLY(AMIDES)						
Nylon, Type 8	0	0	24.3-29.7	0	0	11.9-14.5
Versalon 1112 (dimer acid-polyamine)	0	0	19.4-23.3	0	0	9.5-11.4
Versalon 1175	0	0	19.4-23.3	0	0	9.5-11.4
Versamid 100	17.4-21.7	17.4-18.2	19.4-23.3	8.5-10.6	8.5-8.9	9.5-11.4
Versamid 115	17.4-21.7	16.0-20.3	19.4-26.0	8.5-10.6	7.8-9.9	9.5-12.7
Versamid 900	0	0	0	0	0	0
Versamid 930	0	0	19.4-23.3	0	0	9.5-11.4
Versamid 940	0	0	19.4-23.3	0	0	9.5-11.4
ROSIN DERIVATIVES						
Abalyn (methyl abietate)	14.3-22.7	15.1-22.1	20.5-26.0	7.0-11.1	7.4-10.8	10.0-12.7
Abitol (hydroabietyl alcohol)	14.3-21.9	15.1-22.1	20.5-29.7	7.0-10.7	7.4-10.8	10.0-14.5
Alkydol 160	19.4	17.4-22.1	19.4-26.0	9.5	8.5-10.8	9.5-12.7
Amberol F-7 (phenol-formaldehyde modified rosin)	17.4-21.7	16.0-20.1	19.4-22.3	8.5-10.6	7.8-9.8	9.5-10.9
Amberol 750	0	18.2-22.1	19.4-26.0	0	8.9-10.8	9.5-12.7
Amberol 801	17.4-22.7	15.1-20.3	0	8.5-11.1	7.9-9.9	0
Arochem 455 (bisphenol epoxy modified)	0	16.0-27.2	19.4-29.7	0	7.8-13.3	9.5-14.5
Arochem 462	19.4	17.4-22.1	19.4-29.7	9.5	8.5-10.8	9.5-14.5
Cellolyn 21	14.3-22.7	15.1-20.3	20.5-24.3	7.0-11.1	7.4-9.9	10.0-11.9
Cellolyn 95-80T	14.3-22.7	15.1-20.3	20.5-24.3	7.0-11.1	7.4-9.9	10.0-11.9
Cellolyn 102	16.0-20.5	17.4-22.1	20.5-24.3	7.8-10.0	8.5-10.8	10.0-11.9
Cellolyn 104	16.0-20.5	16.0-22.1	20.5-23.3	7.8-10.0	7.8-10.8	10.0-11.4
Cellolyn 502-60X	17.4-22.7	15.1-20.3	20.5-24.3	8.5-11.1	7.4-9.9	10.0-11.9
Cellolyn 582-60X	16.0-22.7	15.1-20.3	20.5-24.3	7.8-11.1	7.4-9.9	10.0-11.9
Dymerex (dimerized rosin)	15.1-21.7	16.0-20.3	19.4-23.3	7.4-10.6	7.8-9.9	9.5-11.4
Ester Gum (glycerol rosin ester)	14.3-21.7	15.1-22.1	19.4-22.3	7.0-10.6	7.4-10.8	9.5-10.9
17% Fumarated rosin	17.4-21.7	15.1-27.2	19.4-29.7	8.5-10.6	7.4-13.3	9.5-14.5
22% Fumarated rosin	18.2-21.7	15.1-27.2	19.4-29.7	8.9-10.6	7.4-13.3	9.5-14.5
Glidden B952	19.4-21.7	15.1-22.1	19.4-26.0	9.5-10.6	7.4-10.8	9.5-12.7
Glidden VBR757	0	17.4-22.1	19.4-29.7	0	8.5-10.8	9.5-14.5
Hercolyn D (methyl hydroabietate)	14.3-24.1	15.1-22.1	20.5-26.0	7.0-11.8	7.4-10.8	10.0-12.7
Lewisol 28 (maleic modified)	16.0-20.5	15.1-20.3	20.5-21.7	7.8-10.0	7.4-9.9	10.0-10.6
Neolyn 23	17.4-22.7	17.4-27.2	0	8.5-11.1	8.5-13.3	0
Neolyn 40	18.2-26.0	17.4-27.2	20.5-26.0	8.9-12.7	8.5-13.3	10.0-12.7
Newport V-40 ( $\alpha$ -pinene resin)	17.4-22.7	15.1-24.8	19.4-29.7	8.5-11.1	7.4-12.1	9.5-14.5
Pentalyn A (pentaerythritol ester of rosin)	17.4-21.7	15.1-20.3	19.4-23.3	8.5-10.6	7.4-9.9	9.5-11.4
Pentalyn C (pentaerythritol ester of rosin)	15.1-21.9	15.1-20.3	20.5-23.3	7.4-10.7	7.4-9.9	10.0-11.4
Pentalyn G (pentaerythritol ester of rosin)	17.4-21.7	16.0-20.3	19.4-22.3	8.5-10.6	7.8-9.9	9.5-10.9
Pentalyn H (pentaerythritol ester of rosin)	14.3-21.9	15.1-20.3	20.5-23.3	7.0-10.7	7.4-9.9	10.0-11.4
Pentalyn K (pentaerythritol ester of rosin)	17.4-21.7	16.0-20.3	19.4-23.3	8.5-10.6	7.8-9.9	9.5-11.4
Pentalyn X (pentaerythritol ester of rosin)	16.0-20.5	15.1-20.3	20.5	7.8-10.0	7.4-9.9	10.0
Pentalyn B25 (pentaerythritol ester of rosin)	17.4-22.7	15.1-20.3	20.5-24.3	8.5-11.1	7.4-9.9	10.0-11.9
Pentalyn 255 (pentaerythritol ester of rosin)	18.2-20.5	15.1-22.1	20.5-29.7	8.9-10.0	7.4-10.8	10.0-14.5
Pentalyn 802A (pentaerythritol ester of rosin)	16.0-20.5	15.1-20.3	0	7.8-10.0	7.4-9.9	0
Pentalyn 830 (pentaerythritol ester of rosin)	17.4-19.4	16.0-22.1	19.4-23.3	8.5-9.5	7.8-10.8	9.5-11.4
Pentalyn 833 (pentaerythritol ester of rosin)	17.4-21.9	15.1-20.3	22.3	8.5-10.7	7.4-9.9	10.0
Pentalyn 856 (pentaerythritol ester of rosin)	17.4-22.7	15.1-22.1	19.4-23.3	8.5-11.1	7.4-10.8	9.5-11.4
Pentalyn 954 (pentaerythritol ester of rosin)	16.0-21.9	15.1-20.3	0	7.8-10.7	7.4-9.9	0
Petrex 7-75T	18.2-26.0	17.4-27.2	23.3-29.7	8.9-12.7	8.5-13.3	11.4-14.5
Petrex 130H	16.0-22.7	15.1-16.2	20.5-24.3	7.8-11.1	7.4-7.9	10.0-11.9
Poly-pale ester 1	16.2-21.9	15.1-20.3	20.5-23.3	7.0-10.7	7.4-9.9	10.0-11.4
Poly-pale ester 10	14.3-22.7	15.1-20.3	20.5-24.3	7.0-11.1	7.4-9.9	10.0-11.9
Staybelite ester 5 (glycerol ester hydrogenated rosin)	14.3-21.9	15.1-20.3	20.5-24.3	7.0-10.7	7.4-9.9	10.0-11.9
Staybelite ester 10 (glycerol ester hydrogenated rosin)	14.3-21.9	15.1-20.3	20.5-24.3	7.0-10.7	7.4-9.9	10.0-11.9
Vinsol (oxygenated rosin)	21.7-29.3	16.0-27.2	19.4-26.0	10.6-11.9	7.8-13.3	9.5-12.7

Polymer	$\delta$ in [(MPa) <sup>1/2</sup> ] Solvent Hydrogen Bonding			$\delta$ in [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ] Solvent Hydrogen Bonding		
	Poor	Moderate	Strong	Poor	Moderate	Strong
WW Gum rosin	17.4-22.7	15.1-22.1	19.4-23.3	8.5-11.1	7.4-10.8	9.5-11.4
Wood Rosin M grade	15.1-21.7	15.1-22.1	19.4-29.7	7.4-10.6	7.4-10.8	9.5-14.5

## POLY(STYRENE) AND COPOLYMERS

Amoco 18-290	17.4-21.7	17.4-20.3	0	8.5-10.6	8.5-9.9	0
Bakelite's RMD4511 (S/An)	21.7-22.7	19.0	0	10.6-11.1	9.3	0
Buton 100 (S/B)	14.3-21.7	15.1-20.3	0	7.0-10.6	7.4-9.9	0
Buton 300 (S/B)	17.4-21.7	15.1-20.3	19.4-21.5	8.5-10.6	7.4-9.9	9.5-10.5
Koppers KTPL-A (poly(styrene))	16.4-21.7	16.6-20.3	0	8.0-10.6	8.1-9.9	0
Lustrex "High Test 88" (rubber-modified polystyrene)	17.4-21.7	19.0	0	8.5-10.6	9.3	0
Lyttron 810	24.3	20.3-30.1	0	11.0	9.9-14.7	0
Lyttron 820	19.4	18.2-30.1	22.3-29.7	9.5	8.9-14.7	10.9-14.5
Marbon 9200 (S/B)	17.4-21.7	19.0-20.3	0	8.5-10.6	9.3-9.9	0
Parapol S-50	19.4	16.0	0	9.5	7.8	0
Parapol S-60	19.4	16.0	0	9.5	7.8	0
Piccoflex 120	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Shell X-450	19.4-21.7	17.4-24.8	19.4-26.0	9.5-10.6	8.5-12.1	9.5-12.7
SMA 1430A	24.1	17.4-27.0	19.4-29.7	11.8	8.5-13.2	9.5-14.5
85% Styrene/15% acrylamide	0	0	0	0	0	0
85% Styrene/15% acrylonitrile	18.2-22.7	19.0-24.8	0	8.9-11.1	9.3-12.1	0
85% Styrene/15% butanol	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
82% Styrene/18% cyclo	19.4	17.4-22.1	0	9.5	8.5-10.8	0
81% Styrene/11% 2-ethyl hexyl acrylate/8% acrylic acid	18.2-21.7	16.0-20.3	0	8.9-10.6	7.8-9.9	0
90% Styrene/10% methacrylic acid	19.4-21.7	17.4-22.1	0	9.5-10.6	8.5-10.8	0
85% Styrene/15% methyl acrylate	17.4-22.7	16.0-24.8	0	8.5-11.1	7.8-12.1	0
60% Styrene/40% methyl half ester of maleic acid	0	17.4-27.0	21.5-23.3	0	8.5-13.2	10.5-11.4
57% Styrene/43% propyl half ester of maleic acid	18.2-24.1	17.4-27.0	19.4-23.3	8.9-11.8	8.5-13.2	9.5-11.4
85% Styrene/15% vinyl butyl ether	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Styron 440M-27 (modified polystyrene)	17.4-21.7	19.0	0	8.5-10.6	9.3	0
Styron 475M-27	17.4-21.7	19.0	0	8.5-10.6	9.3	0
Styron 480-27	19.4-21.7	19.0	0	9.5-10.6	9.3	0

## VINYL POLYMERS

Acryloid K120N	17.4-26.0	17.4-27.0	0	8.5-12.7	8.5-13.2	0
DODA 3457	17.4-19.0	0	0	8.5-9.5	0	0
DODA 6225	17.4-19.4	0	0	8.5-9.5	0	0
Elvax 150 (PVAc/E)	16.0-21.7	0	0	7.8-10.6	0	0
Elvax 250 (PVAc/E)	17.4-19.4	0	0	8.5-9.5	0	0
Elvax EOD 3602-1	16.0-21.7	16.0-17.4	0	7.8-10.6	7.8-8.5	0
Exon 470	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Exon 471	17.4-22.7	16.0-24.8	0	8.5-11.1	7.8-12.1	0
Exon 473	17.4-22.7	16.0-20.3	0	8.5-11.1	7.8-9.9	0
Geon 121 (poly(vinyl chloride))	21.7-22.7	19.0-20.3	0	10.6-11.1	9.3-9.9	0
Polycyclo	0	18.2-22.1	19.4-29.7	0	8.9-10.8	9.5-14.5
Poly(vinyl butyl ether)	16.0-21.7	15.1-20.3	19.4-23.3	7.8-10.6	7.4-9.9	9.5-11.4
Poly(vinyl ethyl ether)	14.3-22.7	15.1-22.1	19.4-29.7	7.0-11.1	7.4-10.8	9.5-14.5
Poly(vinyl formal) (7/70E)	0	20.3-27.2	0	0	9.9-13.3	0
Poly(vinyl formal) (15/95E)	0	20.3-27.2	0	0	9.9-13.3	0
Poly(vinyl isobutyl ether)	14.3-21.7	15.1-20.3	19.4-23.3	7.0-10.6	7.4-9.9	9.5-11.4
Saran F-120 (poly(vinylidene chloride) copolymer)	19.4-22.7	24.8-30.1	0	9.5-11.1	12.1-14.7	0
Saran F-220 (poly(vinylidene chloride))	19.4-22.7	22.1-30.1	0	9.5-11.1	10.8-14.7	0
Shawinigan RS3512 (30% hydrolysed PVAc)	0	0	0	0	0	0
Shawinigan RS3648 (30% hydrolysed PVAc)	22.7-26.0	22.1-30.1	26.0-29.7	11.1-12.7	10.8-14.7	12.7-14.5
Sinclair 3840A	18.2-19.4	16.4-20.3	20.5-23.5	8.9-9.5	8.0-9.9	10.0-11.5
Tedlar (poly(vinyl fluoride))	0	0	0	0	0	0
63 VAc/33 EHA/4 MAA	0	17.4-20.3	0	0	8.5-9.9	0
76 VAc/12 EHA/8 C/4 MAA	0	19.0-27.2	0	0	9.3-13.3	0
70 VAc/20 EA/10 Cyclo	18.2-26.0	16.0-30.1	19.4-29.7	8.9-12.7	7.8-14.7	9.5-14.5
46 VBE/27 An/27 mAm	24.1	18.2-22.1	0	11.8	8.9-10.8	0
46 VBE/27 MA/27 mAm	22.9-26.0	18.2-28.4	21.5-29.7	11.2-12.7	8.9-13.9	10.5-14.5
75 Vinylidene chloride/25 acrylic acid	0	17.4-25.0	19.4-29.7	0	8.5-12.2	9.5-14.5



Polymer	$\delta$ in [(MPa) <sup>1/2</sup> ] Solvent Hydrogen Bonding			$\delta$ in [(cal/cm <sup>3</sup> ) <sup>1/2</sup> ] Solvent Hydrogen Bonding		
	Poor	Moderate	Strong	Poor	Moderate	Strong
Vynlite AYAA (poly(vinyl acetate))	18.2-26.0	17.4-30.1	29.7	8.9-12.7	8.5-14.7	14.5
Vynlite VAGH (3% hydrolysed PVAc)	21.7-22.7	16.0-20.3	0	10.6-11.1	7.8-9.9	0
Vynlite VMCH (VAc/maleic copolymer)	21.7-22.7	16.0-24.8	0	10.6-11.1	7.8-12.1	0
Vynlite VXCC	19.4-22.7	16.0-27.0	0	9.5-11.1	7.8-13.2	0
Vynlite VYHH (poly(vinyl chloride-co-acetate))	19.0-22.7	16.0-27.1	0	9.3-11.1	7.8-13.3	0
Vynlite VYLF (poly(vinyl chloride-co-acetate))	19.4-22.7	16.0-27.0	0	9.5-11.1	7.8-13.2	0
Vynlite XYHL (poly(vinyl butyral))	0	18.2-22.1	19.4-29.7	0	8.9-10.8	9.5-14.5
Vynlite XYSG (poly(vinyl butyral))	0	18.2-22.1	19.4-29.7	0	8.9-10.8	9.5-14.5
Vyset 69	18.2-19.4	17.4-20.3	0	8.9-9.5	8.5-9.9	0
MISCELLANEOUS						
Acrylamide monomer	22.7-26.0	22.1-30.1	19.4-29.7	11.1-12.7	10.8-14.7	9.5-14.5
Bakelite P-47 (sulfone resin)	21.7	20.3	0	10.6	9.9	0
Beckolin #27 (modified oil)	14.3-22.7	15.1-20.3	19.4-23.3	7.0-11.1	7.4-9.9	9.5-11.4
Carbowax 4000 (poly(ethylene oxide))	18.2-26.0	17.4-30.1	19.4-29.7	8.9-12.7	8.5-14.7	9.5-14.5
Chlorinated rubber	17.4-21.7	16.0-22.1	0	8.5-10.6	7.8-10.8	0
Conoco H-35	14.3-22.7	15.1-20.3	19.4-23.3	7.0-11.1	7.4-9.9	9.5-11.4
Dammar gum (dewaxed)	17.4-21.7	16.0-20.3	19.4-22.3	8.5-10.6	7.8-9.9	9.5-10.9
Epocryl E-11	26.0	20.3	21.5	12.7	9.9	10.5
Estane X-7	0	20.3	0	0	9.9	0
Hexadecyl monoester of TMA	0	18.2-27.0	19.4-29.7	0	8.9-13.2	9.5-14.5
Hydrogenated sperm oil WX135	18.2-21.7	0	0	8.9-10.6	0	0
Hypalon 20 (chlorosulfonated poly(ethylene))	16.6-20.1	17.2-18.0	0	8.1-9.8	8.4-8.8	0
Hypalon 30 (chlorosulfonated poly(ethylene))	17.4-21.7	16.0-17.4	0	8.5-10.6	7.8-8.5	0
Ketone resin S588 (poly(butanone-2))	21.7-26.0	17.4-27.0	19.4-29.7	10.6-12.7	8.5-13.2	9.5-14.5
Lexan 100 polycarbonate resin	19.4-21.7	19.0-20.3	0	9.5-10.6	9.3-9.9	0
Lexan 105 polycarbonate resin	19.4-21.7	19.0-20.3	0	9.5-10.6	9.3-9.9	0
Modaflow	15.1-22.7	15.1-20.3	19.4-23.3	7.4-11.1	7.4-9.9	9.5
Petrex (acid-dibasic terpene)	19.4-22.7	17.4-25.0	0	9.5-11.1	8.5-12.2	0
Resin #510 (fossil coal resin)	15.1-21.7	15.1-19.0	19.4	7.4-10.6	7.4-9.3	9.5
Santolite MHP (p-toluenesulfonamide-formaldehyde)	21.7-26.0	16.0-30.1	19.4	10.6-12.7	7.8-14.7	9.5
Shell polyaldehyde resin EX39 (poly(acrolein))	18.2-22.7	19.0-27.2	0	8.9-11.1	9.3-13.3	0
Shell polyaldehyde resin EX40 (poly(acrolein))	18.2-22.7	19.0-27.2	0	8.9-11.1	9.3-13.3	0
Shellac (pale-pale)	0	20.3-22.1	19.4-29.7	0	9.9-10.8	9.5-14.5
Silicone DC-23	15.1-17.4	15.1-16.0	19.4-20.5	7.4-8.5	7.4-7.8	9.5-10.0
Silicone DC-1107	14.3-19.4	19.0-22.1	19.4-23.3	7.0-9.5	9.3-10.8	9.5-11.4
Silicone intermediate Z6018	17.4-22.7	16.2-25.0	20.5-23.3	8.5-11.1	7.9-12.2	10.0-11.4
Sylkyd 50	14.3-26.0	16.2-26.4	19.4-29.7	7.0-12.7	7.9-12.9	9.5-14.5
Soy oil	14.3-22.7	15.1-22.1	19.4-24.3	7.0-11.1	7.4-10.8	9.5-11.9
Soy oil, blown	14.3-22.7	15.1-22.1	19.4-26.0	7.0-11.1	7.4-10.8	9.5-12.7
p-Toluene sulfonamide	24.1	20.3-30.1	26.0-29.7	11.8	9.9-14.7	12.7-14.5

## Identification of Monomer Symbols in Table 3.4

AGE	Allyl glycidyl ether	MA	Maleic anhydride
Am	Acrylamide	MAA	Methacrylic acid
An	Acrylonitrile	mAm	Methylol acrylamide
B	Butadiene	MMA	Methyl methacrylate
tBAMA	tert-Butylamino methacrylate	PE	Pentaerythritol
BMA	Butyl methacrylate	PET	Poly(ethylene terephthalate)
C	Cyclol (bicyclo-2,2-1-hept-5-ene-2-methanol)	PG	1,2-Propane glycol
DEG	Diethylene glycol	PVAc	Poly(vinyl acetate)
DHC	Dehydrated castor oil	S	Styrene
EA	Ethyl acrylate	TEG	Triethylene glycol
E	Ethylene	TMA	Trimellitic glycol
EG	Ethylene glycol	VAc	Vinyl acetate
EHA	Ethylhexyl acrylate	VBE	Vinyl butyl ether
EMA	Ethyl methacrylate		

TABLE 3.5 SINGLE-VALUE SOLUBILITY PARAMETERS OF POLYMERS

Polymer	$\delta[(\text{MPa})^{1/2}]$	$\delta[(\text{cal}/\text{cm}^3)^{1/2}]$	Method	$T^\circ\text{C}$	Refs.
POLY(DIENES)					
Poly(butadiene)	14.65	7.16	calc.		28
	17.19	8.40			66
	17.09	8.35			110
	17.15	8.38	calc.		112
	17.2–17.6	8.4–8.6	obs.		112
	16.6	8.1			118
	17.6	8.6			72
	16.2 ± 0.2	7.9 ± 0.1	IPGC	75	70
(emulsion)	17.19	8.40			79
(sodium)	17.60	8.60			79
	16.6	8.1	calc.		62
	17.09	8.35			104
hydrogenated	16.6	8.1	swelling		75
	16.47	8.05			75
	16.6	8.1	av.		75
Poly(butadiene-co-acrylonitrile)					
BUNA N (82/18)	17.90–17.72	8.75–8.66			19
(80/20)	18.4	9.0	calc.		66
	19.4	9.5	obs.		66
BUNA N (72/25)	18.93	9.25	calc.	25	112
	19.19	9.38	obs.		42
	19.4	9.5	obs.		104
	18.2	8.9			118
	19.4	9.5			79
(70/30)	20.26–20–11	9.90–9.83			19
	19.19	9.38			43
(61/39)	21.1	10.3			19
	21.38–21.28	10.45–10.40			19
	20.5 ± 0.6	10.0 ± 0.3	IPGC	75	70
Poly(butadiene-co-styrene)					
BUNA S (94/4)	16.64–16.45	8.13–8.04			19
(90/10)	17.13	8.37			110
(87.5/12.5)	16.57–16.39	8.10–8.01			19
	16.55	8.09			43
	17.6	8.6			104
	17.31	8.46			112
(85/15)	17.19	8.40			110
	17.35	8.48	calc.		112
	17.4	8.5	obs.		112
	17.39	8.50			79
	17.41	8.51	calc.		66
	17.39	8.50	obs.		66
	17.50	8.55			104
(75/25)	17.29	8.45			110
	17.47	8.54	calc.		112
	16.55	8.09	obs. (lit)		112
	16.49	8.06	obs. (lit)		112
	16.6	8.1			118
	17.50	8.55			79
	17.56	8.58	calc.		66
	17.50	8.55	obs.		66
	17.60	8.60			104
(71.5/28.5)	16.72–16.55	8.17–8.09			19
	17.51	8.56			112
(70/30)	17.35	8.48			110
(60/40)	17.50	8.55			110
	17.70	8.65	calc.		112
	17.74	8.67	obs.		112
	17.74	8.67			79
	17.76	8.68	calc.		66
	17.74	8.67	obs.		66
	17.80	8.70			104

Polymer	$\delta[(\text{MPa})^{1/2}]$	$\delta[(\text{cal}/\text{cm}^3)^{1/2}]$	Method	$T^\circ\text{C}$	Refs.
Poly(butadiene-co-vinylpyridine) (75/25)	19.13	9.35			
Poly(chloroprene)	18.42	9.00			79
	16.59	8.11		25	110
	19.19	9.38	calc.		28
	16.74	8.18	calc.		112
	18.93	9.25	obs.		42
	17.6	8.6	obs.		104
	16.8	8.2			118
	18.8	9.2			44
	16.76	9.2			72
	17.6	8.19			79
	17.74-17.54	8.6	swelling		43
	15.18	8.67-8.57			19
Poly(isoprene)	18.0 $\pm$ 0.4	8.0 $\pm$ 0.2	IPGC	75	19
1,4-cis					70
	15.18	7.42			
	16.64	8.13	calc.	25	28
	16.68	8.15			42
	16.57	8.10		25	74
	20.46	10.0		35	74
	16.57	8.10	swelling	35	74
	16.47	8.05	av.	35	74
	16.57	8.10	swelling	35	74
	16.68	8.15	swelling	35	74
	16.6	8.1	calc.	35	74
	16.4	8.0	swelling		75
	16.47	8.05			76
	16.82	8.22	av.		76
	16.68	8.15		25	110
	16.2	7.9	calc.	25	112
	16.33	7.98	obs.		112
	17.09	8.35	obs.		112
natural rubber	16.2	7.9	obs.		112
	16.2	7.9			72
	16.6	8.1			43
	16.68	8.15			19
	17.09	8.35			112
	17.0	8.3			104
	16.6	8.1			124
	16.4	8.0			118
	17.09	8.35			19,104
	16.33	7.98			79
	16.6	8.1			43
Gutta percha	16.49-16.42	8.06-8.12			19
chlorinated	16.6	8.1			19
	19.2	9.4	calc.		73
					21-24
POLY(ALKENES)					
Poly(ethylene)	15.76	7.70			
	16.6	8.1			110
	16.0	7.8	calc.		112
	16.2	7.9			58
	17.09	8.35			97
	16.4	8.0			8
	16.2	7.9	calc.		124
	16.2	7.9			118
	16.8	8.2			72
	16.2	7.9	calc.		97
	17.99	8.79	obs.		73
Poly(ethylene-co-vinyl acetate)	18.6 $\pm$ 0.9	9.1 $\pm$ 0.4	IPGC	25	119
Poly(isobutene)	17.0 $\pm$ 0.4	8.3 $\pm$ 0.2	IPGC	75	71
	14.5	7.1	calc.		70
	16.06	7.85	av.		28
	16.0	7.8		35	74
	16.47	8.05	swelling		74
			swelling		74

Polymer	$\delta[(\text{MPa})^{1/2}]$	$\delta[(\text{cal}/\text{cm}^3)^{1/2}]$	Method	$T^\circ\text{C}$	Refs.
Poly(isobutene) <i>cont'd</i>	16.25	7.94			19,104
	16.06	7.85		25	110
	15.76	7.70	calc.		112
	16.47	8.05	obs.		112
	16.4	8.0			58
	16.47	8.05			104
	16.6	8.1			21-24
	16.0	7.8			19
	17.0	8.3	calc.		124
	16.47	8.05			72
Poly(isobutene-co-isoprene) butyl rubber	16.47	8.05			79
	16.06-15.90	7.85-7.77			19
	16.47	8.05			104
	15.76	7.70			112
Poly(methylene)	14.3	7.0	extrap.	20	45
Poly(propylene)	18.8	9.2		25	58
	19.2	9.4	calc.		124
POLY(ACRYLICS) AND POLY(METHACRYLICS)					
Poly(acrylic acid)					
—, butyl ester	18.0	8.8		35	75
	18.01	8.80	av.		75
	18.52	9.05	swelling		75
	17.4	8.5	calc.		75
	18.6	9.1	swelling		77
	18.52	9.05			77
	19.77	9.66	calc.		119
—, ethyl ester	19.13	9.35	av.		75
	19.2	9.4	swelling		75
	19.8	9.7	calc.		75
	19.2	9.4	swelling		77
	19.13	9.35			77
	19.19	9.38			45
	18.8	9.2	calc.		62
	20.40	9.97	calc.		119
—, isobornyl ester	16.8	8.2	calc.		62
—, methyl ester	20.7	10.1	av.		75
	20.77	10.15	swelling		75
	20.1	9.8	calc.		75
	20.77	10.15	swelling		77
	21.3	10.4			77
—, propyl ester	20.7	10.1	swelling		77
	18.52	9.05			75
	18.42	9.00	av.		75
	18.4	9.0	calc.		75
Poly(acrylonitrile)	25.27	12.35	calc.		119
	25.6	12.5			66
	26.09	12.75	calc.	25	112
	31.5	15.4			118
Poly( $\alpha$ -chloroacrylic acid) methyl ester	20.7	10.1	calc.		112
Poly(methacrylic acid)					
—, butyl ester	17.90	8.75	swelling		77
	17.8	8.7			77
	18.01	8.80	swelling		77
	17.90	8.75			77
	17.0	8.3	calc.		73
	14.7	7.2	IPGC	140	31
—, isobutyl ester	14.7	7.2	IPGC	140	31
—, sec-butyl ester	14.7	7.2	IPGC	140	31
—, ethoxyethyl ester	18.4	9.0	swelling		77
	20.3	9.9			77
—, ethyl ester	18.31	8.95	swelling		77
	18.2	8.9			77
	18.6	9.1	calc.		73

Polymer	$\delta[(\text{MPa})^{1/2}]$	$\delta[(\text{cal}/\text{cm}^3)^{1/2}]$	Method	T°C	Refs.
Poly(methacrylic acid) <i>cont'd</i>					
—, n-hexyl ester	17.6	8.6	calc.		73
—, isobornyl ester	16.6	8.1			62
—, lauryl ester	16.8	8.2	calc.		73
—, methyl ester	18.58	9.08		25	19
	18.66–18.52	9.12–9.05			19
	19.4	9.5	swelling		77
	19.34	9.45			77
	26.27	12.84			110
	18.93	9.25	calc.		112
	18.4–19.4	9.0–9.5			7
	18.58	9.08			118
	19.50	9.53	calc.		119
—, octyl ester	17.2	8.4	calc.		73
—, propyl ester	18.0	8.8	calc.		73
—, stearyl ester	16.0	7.8	calc.		73
Poly(methacrylonitrile)	21.0	10.7			118
	21.9	10.7	calc.		112
POLY(VINYL HALIDES), POLY(VINYL ALCOHOL), POLY(VINYL ESTER)					
Poly(tetrafluoroethylene)	12.7	6.2	calc.		112
	12.7	6.2			118
Poly(vinyl acetate)	19.62	9.56	calc.	25	28
	19.13	9.35		35	78
	20.93	10.23	calc.		119
	19.2	9.40	Small's method		78
	18.0	8.80	lit.		78
	22.61	11.05		25	110
	19.2	9.4	calc.		112
	19.2	9.4			118
Poly(vinyl acetate-co-vinyl alcohol)	21.94	10.72	calc.		119
Poly(vinyl alcohol)	25.78	12.60			110
Poly(vinyl bromide)	19.42	9.49			34
	19.6	9.6	calc.		112
Poly(vinyl chloride)	19.34–19.19	9.45–9.38			19
	19.28	9.42	calc.		28
	20.67	10.10			110
	19.54	9.55	calc.		112
	19.8	9.7	obs.		72
	19.2	9.4			19
	19.8	9.7			21–24
	22.1	10.8			58
	20.1	9.8			124
	19.50	9.53			118
	19.8	9.7			72
	20.32	9.93	calc.		119
Poly(vinyl chloride), chlorinated	19.0	9.3	visc.	25	117
Poly(vinyl chloride-co-vinyl acetate) (87/13)	21.7	10.6	calc.		28
	21.3	10.4			21–24
(VYHH)	20.42	9.98	calc.		119
Poly(vinyl chloride-co-vinyl acetate-co-maleic acid)	20.44	9.99	calc.		119
Poly(vinyl chloride-co-vinyl acetate-co-vinyl alcohol)	20.77	10.15	calc.		119
Poly(vinylidene chloride)	25.0	12.2			21–24
Poly(vinylidene cyanide-co-vinyl acetate)	22.67	11.08	calc.		128
Poly(vinyl propionate)	18.01	8.80		35	78
	18.52	9.05	Small's method		78
POLY(STYRENES)					
Poly(styrene)	17.52	8.56			19
	17.58–17.45	8.59–8.53			19
	20.16	9.85	calc.		28
	17.86–17.92	8.73 or 8.76			48
	17.84, 18.56	8.72 or 9.07	visc.		116
	18.6	9.1			66

Polymer	$\delta[(\text{MPa})^{1/2}]$	$\delta[(\text{cal}/\text{cm}^3)^{1/2}]$	Method	$T^\circ\text{C}$	Refs.
Poly(styrene) <i>cont'd</i>					
	18.72	9.15		35	74
	18.62	9.10	av.		74
	18.62	9.10	swelling		74
	18.66	9.12	calc.		74
	19.09	9.33		25	110
	18.66	9.12	calc.		112
	18.6	9.1	obs. (lit)		112
	17.6-19.8	8.6-9.7	obs. (lit)		112
	17.4	8.5			18
	17.6	8.6			19
	18.4	9.0			58
	19.28	9.42	calc.		119
	21.1	10.3	calc.		124
	17.52	8.56			118
	17.84	8.72			19,97
	18.6	9.1			104
	17.6-17.8	8.6-8.7			72
	18.6	9.1			79
Poly(styrene-co-divinylbenzene)	15.6	7.6	IPGC	140	31
	18.6	9.1	obs. (lit)		112
	17.39	8.50			18
Poly(styrene-co-n-butyl methacrylate)	15.1	7.4	IPGC	140	31
Poly(styrene-co-iso-butyl methacrylate)	15.1	7.4	IPGC	140	31
Poly( $\alpha$ -methylstyrene-co-acrylonitrile)	16.4	8.0	IPGC	180	111
OTHER COMPOUNDS					
Alkyd, medium oil length	19.2	9.4			21-24
Epoxy resin	22.3	10.9			118
Poly(imino-hexamethyleneimino-adipoyl)	27.8	13.6			118
Poly(oxydimethylsilylene)	15.04	7.35			110
	14.9	7.3	obs.	21-24	76
	15.45	7.55	swelling		76
	15.6	7.6	av.		76
	14.9	7.3			118
	15.59	7.62			45
Poly(oxyethylene)	15.4	7.5		25	125
Poly(oxyethyleneoxyterephthaloyl)	20.2 $\pm$ 2	9.9 $\pm$ 1	IPGC	25	31
	21.9	10.7			118
Poly(oxytrimethylene) Poly(oxetane)	21.9	10.7	calc.		112
—, 3,3-dimethyl	19.2	9.4	visc.	25	31
—, 3,3-diethyl	16.2	7.9	visc.	25	92
Poly(thioethylene)	16.2	7.9	visc.	25	92
	19.23	9.40			110
	19.19	9.38	swelling		43
Poly(thiophenylethylene)	18.4	9.0	swelling		43
Poly(urethane) (unknown composition)	19.0 $\pm$ 1.0	9.3 $\pm$ 0.5			87
	20.5	10.0	swelling		76
	20.5	10.0	av.		76
CELLULOSE AND DERIVATIVES					
Benzyl cellulose	25.23	12.33			110
Cellulose	32.02	15.65			110
Cellulose acetate (56% ac. groups)	27.83	13.60			110
(48% ac. groups)	27.19	13.29			110
Cellulose diacetate	23.22	11.35	calc.		112
	22.3	10.9			118
Cellulose nitrate	22.3	10.9			72
(11.83% N)	30.39	14.85			110
	21.44	10.48	calc.		112
	21.7	10.6			72
(11.4% N)	23.5	11.5			21-24
Ethyl cellulose	21.93	10.72			72
	21.1	10.3			21-24

TABLE 3.6 HANSEN SOLUBILITY PARAMETERS OF POLYMERS

Polymer (Trade Name, Supplier)	Solubility Parameter [(MPa) <sup>1/2</sup> ]				Refs.
	$\delta_D$	$\delta_P$	$\delta_H$	$\delta$	
Acrylonitrile-butadiene elastomer (Hycar 1052, BFGoodrich)	18.6	8.8	4.2	21.0	56
Alcohol soluble resin (Pentalyn 255, Hercules)	17.5	9.3	14.3	24.4	56
Alcohol soluble rosin resin (Pentalyn 830, Hercules)	20.0	5.8	10.9	23.5	56
Alkyd, long oil (66% oil length, Plexal P65, Polyplex)	20.42	3.44	4.56	21.20	56
Alkyd, short oil (coconut oil 34% phthalic anhydride; Plexal C34)	18.50	9.21	4.91	21.24	56
Blocked isocyanate (phenol, Suprasec F5100, ICI)	20.19	13.16	13.07	27.42	56
Cellulose acetate (Cellidore A, Bayer)	18.60	12.73	11.01	25.08	56
Chlorinated polypropylene (Parlon P10, Hercules)	20.26	6.32	5.40	21.89	56
Coumarone-indene resin (Piccoumarone 450L, Penn. Ind. Chem.)	19.42	5.48	5.77	20.99	56
Epoxy (Epikote 1001, Shell)	20.36	12.03	11.48	26.29	56
Ester gum (Ester gum BL, Hercules)	19.64	4.73	7.77	21.65	56
Furfuryl alcohol resin (Durez 14383, Hooker Chemical)	21.16	13.56	12.81	28.21	56
Hexamethoxymethyl melamine (Cymel 300, American Cyanamid)	20.36	8.53	10.64	24.51	56
Isoprene elastomer (Cariflex IR305, Shell)	16.57	1.41	-0.82	16.65	56
Cellulose	12.69	***	22.30	25.66	81
Cellulose acetate	15.55	***	11.87	19.56	81
Cellulose acetate butyrate	15.75	***	8.59	17.94	81
Cellulose acetate propionate	15.75	***	10.23	18.78	81
Cellulose nitrate (1/2 sec; H-23, Hagedon)	15.41	14.73	8.84	23.08	56
Cellulose triacetate	15.55	***	10.64	18.84	81
Cellulose tridecanoate	19.85	***	6.14	20.77	81
Nylon 4	19.44	***	14.12	24.02	81
Nylon 66	18.62	5.11	12.28	22.87	98
(Zytel, Dupont)	18.62	0.00	14.12	23.37	56
Pentaerythritol ester of rosin, modified (Cellolyn 102, Hercules)	21.73	0.94	8.53	23.37	56
Petroleum hydrocarbon resin (Piccopale 110, Penn. Ind. Chem.)	17.55	1.19	3.60	17.96	56
Phenolic resin (resole, Phenodur 373U Chemische Werke Albert)	19.74	11.62	14.59	27.15	56
Phenolic resin, pure (Super Beckacite 1001, Reichhold)	23.26	6.55	8.35	25.57	56
Poly(acrylonitrile)	18.21	16.16	6.75	25.27	98
Polyamide, thermoplastic (Versamid 930, General Mills)	17.43	-1.92	14.89	23.02	56
cis-Poly(butadiene) elastomer (Bunahuls CB10, Chemische Werke Huels)	17.53	2.25	3.42	18.00	56
Poly(butadiene)	16.98	***	1.02	17.02	98
Poly(isobutylene) (Lutonal IC/123, BASF)	14.53	2.52	4.66	15.47	56
Poly(ethyl methacrylate) (Lucite 2042, Du Pont)	17.60	9.66	3.97	20.46	56
Poly(ethylene terephthalate)	19.44	3.48	8.59	21.54	98
Poly(methyl methacrylate) (Rohm and Haas)	18.64	10.52	7.51	22.69	56
Poly(propylene) isotactic (Profax 6701, Hercules)	17.19	***	***	17.19	81

Polymer (Trade Name, Supplier)	Solubility Parameter [(MPa) <sup>1/2</sup> ]				Refs.
	$\delta_D$	$\delta_P$	$\delta_H$	$\delta$	
Poly(styrene) (Polystyrene LG, BASF)	21.28	5.75	4.30	22.47	56
Poly(sulfone), Bisphenol A (Udel)	19.03	0.00	6.96	20.26	81
Poly(vinyl acetate) (Mowilith 50, Hoechst)	20.93	11.27	9.66	25.66	56
Poly(vinyl butyral) (Butvar B76, Shawinigan)	18.60	4.36	13.03	23.12	56
Poly(vinyl chloride) Vipla KR, K = 50, Montecatini)	18.23	7.53	8.35	21.42	56
Poly(vinyl chloride)	18.72	10.03	3.07	21.46	33
Poly(vinyl chloride)	18.82	10.03	3.07	21.54	98
Saturated polyester (Desmophen 850, Bayer)	21.54	14.94	12.28	28.95	56
Styrene-butadiene (SBR) raw elastomer (Polysar 5630, Polymer Corp.)	17.55	3.36	2.70	18.07	56
Terpene resin (Piccolyte S-1000, Penn. Ind. Chem.)	16.47	0.37	2.84	16.72	56
Urea-formaldehyde resin (Plastopal H, BASF)	20.81	8.29	12.71	25.74	56

\* \*\*\*, indicates data for which only dispersive and polar contributions are available as in Equation 8.

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